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## CANADIAN ERUCIC ACID OILS

### I. REFINING AND BLEACHING[1]


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### Abstract

Dark colored commercial erucic acid oils from rapeseed, and from mustard seed screenings (*Brassica* species), have been subjected to various refining and bleaching treatments. Superfiltrol bleaching clay was superior to Neutrol clay or an unactivated Manitoba bentonite. Lecithin-free, partially alkali refined, and alkali refined oils were bleached readily by heating for 20 min. at 100° C., as little as 2% clay yielding oils similar in color to commercial table oils. Crude oils could be bleached without preliminary refining treatment if the temperature were raised to 200° C., though some increase in free fatty acid occurred. With Stanolax as a color standard, relative transmissions at a wave length of 440 mμ were 4.5% for crude rapeseed oil, 5.0% for alkali refined rapeseed oil, and 58, 78, and 91%, respectively, for the alkali refined oil bleached with 1, 2, and 4% Superfiltrol. The behavior of mustard seed oils was closely similar though more bleaching clay was required. For both rape and mustard, spectrophotometric analyses indicated generally similar transmissions for crude, lecithin-free, and partially alkali refined oils in the range from 225 to 500 mμ, while fully alkali refined oils showed reduced transmissions in the triene region (260 to 280 mμ) with slightly increased transmission over the range from 320 to 500 mμ. Bleached oils were characterized by high transmissions in the range above 320 mμ.


### Introduction

The erucic acid oils produced in Canada are obtained from rapeseed and from mustard seed varieties (*Brassica* species) screened from the western Canadian wheat crop. The commercially expelled oils are usually very dark in color and generally unattractive in appearance. The undesirable color of rapeseed oil has been attributed to the presence of chlorophyll in the common black Argentine rape grown in Canada where it ripens unevenly. Whatever the cause, improvement in color is a necessary antecedent to any edible use and to most industrial uses.

Although erucic acid oils have been widely used for edible purposes in India and China, their use as food has been relatively inconsequential in North America. Verbal reports had indicated that effective color removal was difficult, alkali refined oils tending to yield green products on hydrogenation. These statements were confirmed by hydrogenation of commercially available refined and bleached rapeseed oil, which developed the reported dis-


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coloration. A study of the recent literature on German wartime technology shows that rapeseed oil was their chief source of edible fat (3). The present world shortage of fats and the possibility of large scale Canadian production of erucic acid oils were among the considerations leading to this study of processing conditions.

## Materials and Methods

Crude rape and mustard oils were obtained from a commercial source in Moose Jaw, Saskatchewan; their general characteristics are given in Table I. These were refined and bleached in various ways, and the resulting oils were examined with special reference to color and free fatty acid.

TABLE I

CHARACTERISTICS OF CRUDE ERUCIC ACID OILS

| | Rapeseed oil | Oil from mustard seed screenings |
|---|---|---|
| Refractive index, 25° C. | 1.4715 | 1.4735 |
| Saponification value | 179 | 188 |
| Free fatty acid content (as oleic), % | 0.4 | 0.5 |
| Iodine value | 103 | 118 |
| Color | | |
| F.A.C. Standard Colors, not darker than number | 21 | 27 |
| Relative transmission with Stanolax as standard in Evelyn photoelectric colorimeter, % transmission at | | |
| 440 mμ | 4.5 | 4.8 |
| 660 mμ | 32.5 | 15.0 |

Conventional alkali refining was conducted in accordance with A.O.C.S. procedures set down for the refining of soybean oils (1). Partial alkali refining involved a similar procedure with the use of an amount of 6% sodium hydroxide solution stoichiometrically equivalent to the free fatty acid content; these oils are hereafter referred to as 'alkali treated'.

A number of rapeseed oil samples were processed as follows: alkali refined by conventional methods; subjected to five water washings at 100° C. to remove lecithin in accordance with reported German procedure (3); alkali treated to yield an oil of about the same free fatty acid content as the lecithin-free sample; and subjected to steam distillation for one hour at 200° C. The mustard seed oil was subjected to alkali treatment and to conventional alkali refining.

The bleaching clays used were two activated, commercial preparations, Superfiltrol and Neutrol (from the Filtrol Corporation, Los Angeles, Calif.), and a Pembina Manitoba bentonite, which was unactivated. The moisture contents of these clays varied from 3.1 to 4.2%. A few trials made use of the American Oil Chemists Society's official Fuller's earth.

The bleaching operation was conducted in equipment comprised of three heating mantles furnished with 500 ml. three-necked flasks. Each experiment was made on 100 gm. of oil. Bleaching clay was added to the cold oil and the free space of the flask flushed with carbon dioxide throughout the heating period. Heating of the mantles was controlled by means of variable transformers set to bring the temperature to the desired point in approximately 10 min., and manually controlled thereafter. Stated temperatures were maintained within ± 3° C. When the desired heating period had elapsed, the mantle was lowered, stirring stopped, and the oil filtered rapidly by suction through a Büchner funnel. Oil samples were stored under an atmosphere of carbon dioxide in ordinary glass bottles in the diffuse light of the laboratory.

Spectrophotometric absorption curves were made on both crude and refined oils with the Model D-11 Beckman instrument, 1 gm. of oil being made up to a volume of 500 ml. with normal heptane and an aliquot taken for measurement in a 1 cm. quartz cuvette. The color of crude, refined, and variously bleached oils was compared by means of the Evelyn photoelectric colorimeter, with Stanolax, a white mineral oil, as the reference medium. Relative transmissions were determined at wave lengths of 440 and 660 m$\mu$, respectively. These wave lengths were selected because it has been shown that chlorophylls A and B show absorption maxima in these regions (2). The free fatty acid content of oil samples was determined and expressed as per cent oleic acid.

## Results

Spectrophotometric analyses of rape and mustard oils confirmed their general similarity. The curves *A* to *D* of Fig. 1 describe the changes in extinction coefficients over the range from 225 to 500 m$\mu$, for crude, alkali treated, alkali refined, and alkali refined and bleached mustard oils. The alkali refined oil (*C*), compared with the crude oil (*A*), showed higher extinction values in the triene region (260 to 280 m$\mu$), but above 310 m$\mu$ the values fell below those for the crude oil. Extinction coefficients for alkali treated oil (*B*) coincided with those for the crude oil (*A*) until the wave length reached 300 m$\mu$, and thereafter the points fell approximately between those of Curves *A* and *C*. Alkali refined oil bleached with 4% Superfiltrol clay (*D*), in comparison with the unbleached oil (*C*), showed slightly decreased extinction coefficients at 230 to 240 m$\mu$ but increased extinction coefficients at 260 to 280 m$\mu$; otherwise the values were virtually identical to a wave length of 320 m$\mu$. From this point the coefficients fell to an extremely low value, indicating inappreciable absorption beyond 350 m$\mu$.

Closely similar results were obtained from the spectrophotometric examination of rapeseed oil. The crude, the lecithin-free, and the alkali treated oils gave extinction coefficients that differed slightly over the entire range. The alkali refined oil showed enhanced extinction values in the triene region but lower values above 330 m$\mu$. Bleached rape oil followed the pattern already described for bleached mustard oil.

*Bleaching Clays*

It is apparent from the data of Tables II, III, and IV, that Superfiltrol is a better bleaching agent than Neutrol, and very much better than unactivated Pembina Manitoba bentonite. The three clays showed different bleaching

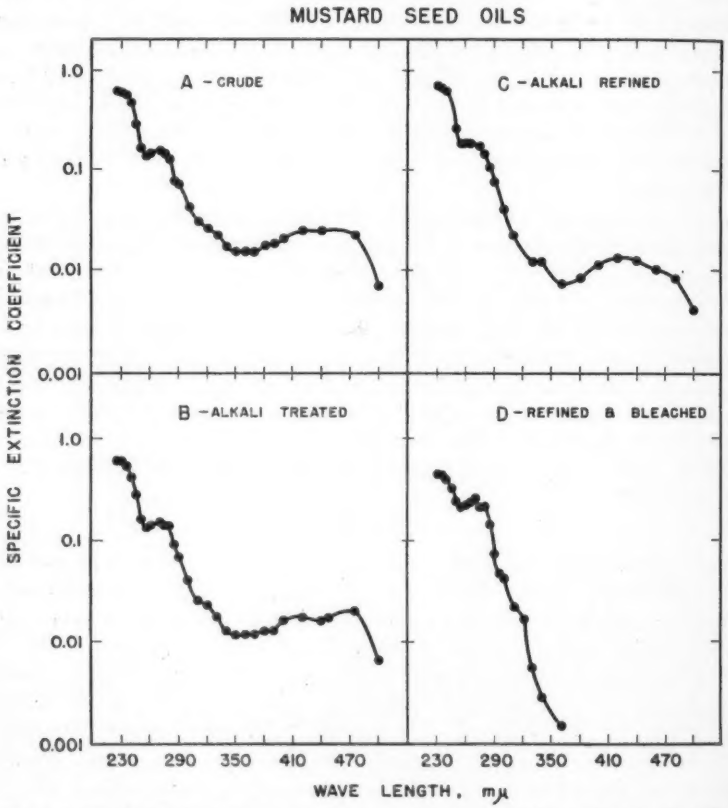


FIG. 1. *Ultraviolet absorption curves for normal heptane solutions of variously refined mustard seed oils.*

properties when judged by transmission at 660 m$\mu$ and the differences were accentuated with transmission at 440 m$\mu$. Also, Superfiltrol did not appear to increase the free acid content when used at 4% for a heating period of 20 min. at 100° C. Superfiltrol was therefore used throughout the remainder of the study.

*Effects of Bleaching Conditions*

The results of Table V (*A*) indicate that increase in the duration of heating from 20 to 80 min. at 100° C. with 4% Superfiltrol had little effect on the relative transmission of the oil. There was some indication that the free

TABLE II

EFFECT OF DIFFERENT CLAYS ON THE BLEACHING OF RAPESEED OIL

(Oil heated for 20 min. at 100° C. with 4% of clay)

| Clay | Crude oil | | | Alkali treated oil | | | Lecithin-free oil | | |
|---|---|---|---|---|---|---|---|---|---|
| | F.F.A., % | Rel. transmission | | F.F.A., % | Rel. transmission | | F.F.A., % | Rel. transmission | |
| | | 660 mμ | 440 mμ | | 660 mμ | 440 mμ | | 660 mμ | 440 mμ |
| None | 0.42 | 32.5 | 4.5 | 0.24 | 39.5 | 4.6 | 0.29 | 32.5 | 4.9 |
| Pembina bentonite | 0.58 | 59.0 | 4.5 | 0.33 | 88.2 | 18.1 | 0.23 | 90.5 | 13.5 |
| Neutrol | 0.40 | 85.8 | 9.8 | 0.32 | 95.0 | 47.3 | 0.20 | 95.2 | 34.1 |
| Superfiltrol | 0.38 | 89.0 | 16.3 | 0.24 | 94.9 | 54.4 | 0.23 | 96.1 | 60.0 |

TABLE III

EFFECT OF DIFFERENT CLAYS ON THE BLEACHING OF OIL FROM MUSTARD SCREENINGS

(Oil heated for 20 min. at 100° C. with 4% clay)

| Clay | Crude oil | | | Alkali treated oil | | |
|---|---|---|---|---|---|---|
| | F.F.A., % | Rel. transmission | | F.F.A., % | Rel. transmission | |
| | | 660 mμ | 440 mμ | | 660 mμ | 440 mμ |
| None* | 0.49 | 15.0 | 4.8 | 0.25 | 18.1 | 4.0 |
| Pembina bentonite | 0.52 | 27.9 | 5.0 | 0.31 | 73.8 | 5.3 |
| Neutrol | 0.50 | 61.0 | 5.0 | 0.19 | 82.9 | 15.0 |
| Superfiltrol | 0.50 | 80.5 | 6.0 | 0.36 | 91.7 | 20.5 |

* *The corresponding oil without any bleach.*

fatty acid content of crude rapeseed oil rose slightly with the longer heating periods, but this was not noted for alkali treated oils.

The results of Tables IV, V (*B*), and VI indicate very marked temperature effects, especially evident for transmissions at 440 mμ, which appeared to pass through a maximum at about 200° C. This effect was noted in the crude rape, steam treated rape, and mustard oils, but not in the alkali treated materials. The crude rape oil subjected to steam treatment (Table IV) showed little change in transmission below 175° C. This sample of oil (bleached at 175° C.) was the only one in the entire investigation that was difficult to filter.

Free fatty acid content tended to increase appreciably with an increase in bleaching temperatures, the effect being substantially greater with crude than with alkali treated oils.

*Effects of Superfiltrol Concentration*

The effects of Superfiltrol over a wide range (2 to 12%) on bleaching for a 20 min. period are illustrated by the data in Tables VII to IX. Crude rape

TABLE IV

EFFECTS OF CLAYS AND TEMPERATURES ON THE BLEACHING OF CRUDE RAPESEED OIL SUBJECTED TO STEAM DISTILLATION FOR ONE HOUR

(Clay at 4% concentration with a 20 min. heating period)

*Effect of different clays, at 100° C.*

| Clay | F.F.A., % | Rel. transmission | |
|---|---|---|---|
| | | 660 mμ | 440 mμ |
| None* | 0.46 | 14.9 | 4.0 |
| Pembina bentonite | 0.35 | 27.0 | 3.8 |
| Neutrol | 0.30 | 40.0 | 4.0 |
| Superfiltrol | 0.29 | 44.7 | 4.2 |

*Effect of temperature of bleaching with Superfiltrol*

| Temp., ° C. | F.F.A., % | Rel. transmission | |
|---|---|---|---|
| | | 660 mμ | 440 mμ |
| 100 | 0.29 | 44.7 | 4.2 |
| 125 | 0.33 | 55.2 | 5.0 |
| 150 | 0.28 | 57.1 | 6.0 |
| 160 | 0.38 | 84.0 | 22.8 |
| 175** | 0.53 | 98.5 | 54.0 |
| 175** | 0.69 | 98.5 | 52.0 |
| 200 | 0.74 | 100.0 | 59.5 |
| 225 | 1.11 | 98.7 | 49.3 |

* *Steam treated rape oil, no bleach.*
** *Duplicates done at different times.*

oil, bleached at a temperature of 200° C. (Table VII), required at least 4% clay to effect substantial improvement in transmission at 440 mμ. As much as 12% Superfiltrol with crude oil yielded products inferior in color to those obtained with 6% clay on the alkali treated and lecithin-free oils. The crude rape oil showed very marked increase in free fatty acid content with increasing concentrations of bleaching clay. Since all samples of alkali treated, lecithin-free, and fully alkali refined oils showed comparatively little change in free fatty acid, the effect on crude oil may be largely attributed to the high bleaching temperature.

The data for alkali treated mustard oil (Table VIII) indicate poorer bleaching than for comparable rape oil (Table VII), the difference being particularly evident for transmissions at 440 mμ. Alkali refined oils (Table IX) showed substantially better bleaching than alkali treated oils (Tables VII and VIII), the extent of the improvement being greater for rape than for mustard. It is interesting to note that 10% Superfiltrol was required with alkali treated mustard oil to equal the bleaching achieved by 4% clay on alkali refined oil.

TABLE V

THE EFFECT OF TIME OF HEATING AND THE EFFECT OF TEMPERATURE ON THE BLEACHING OF RAPESEED OIL

| Condition | Crude oil | | | Alkali treated oil | | |
|---|---|---|---|---|---|---|
| | F.F.A., % | Rel. transmission | | F.F.A., % | Rel. transmission | |
| | | 660 mμ | 440 mμ | | 660 mμ | 440 mμ |
| *A. Effect of time of heating. (Oil heated at 100° C. with 4% Superfiltrol)* | | | | | | |
| Time of heating, min. | | | | | | |
| 20 | 0.38 | 89.0 | 16.3 | 0.24 | 94.9 | 54.4 |
| 40 | 0.56 | 92.0 | 8.2 | 0.18 | 97.0 | 66.0 |
| 60 | 0.56 | 93.0 | 15.5 | 0.20 | 95.0 | 59.3 |
| 80 | 0.62 | 93.0 | 24.8 | 0.18 | 100.0 | 61.0 |
| *B. Effect of temperature. (Oil heated for 20 min. with 4% Superfiltrol)* | | | | | | |
| Temperature, ° C. | | | | | | |
| 100 | 0.38 | 89.0 | 16.3 | 0.24 | 94.9 | 54.4 |
| 125 | 0.35 | 94.8 | 25.8 | 0.23 | 98.5 | 68.0 |
| 150 | 0.47 | 94.0 | 33.5 | 0.28 | 98.0 | 62.0 |
| 175 | 0.50 | 93.2 | 33.8 | 0.90 | 99.0 | 66.3 |
| 200 | 0.57 | 99.0 | 53.5 | 0.70 | 99.1 | 65.0 |
| 225 | 1.07 | 98.0 | 47.7 | — | — | — |
| 250 | 1.61 | 97.2 | 33.0 | — | — | — |

TABLE VI

THE EFFECT OF TEMPERATURE ON THE BLEACHING OF MUSTARD SEED OIL

(Oil heated for 20 min., with 4% Superfiltrol clay)

| Temperature, ° C. | Crude oil | | | Alkali treated oil | | |
|---|---|---|---|---|---|---|
| | F.F.A., % | Rel. transmission | | F.F.A., % | Rel. transmission | |
| | | 660 mμ | 440 mμ | | 660 mμ | 440 mμ |
| 100 | 0.50 | 80.5 | 6.0 | 0.36 | 91.7 | 20.5 |
| 125 | 0.45 | 86.1 | 6.0 | 0.52 | 94.9 | 21.9 |
| 150 | 0.50 | 86.2 | 8.6 | 0.64 | 94.5 | 31.9 |
| 175 | 0.58 | 88.5 | 10.9 | 0.79 | 95.0 | 36.9 |
| 200 | 0.84 | 67.8 | 5.5 | 0.80 | 95.9 | 37.1 |

It is also evident from Table IX that 4% Superfiltrol was required to bleach mustard oil to the extent achieved by 1% with rape oil.

Results of bleaching with 4% Standard Fuller's earth of the American Oil Chemists' Society are included in Table IX for both the rape and mustard seed oils for purposes of comparison.

TABLE VII

EFFECT OF SUPERFILTROL CONCENTRATION ON THE BLEACHING OF RAPESEED OIL

(Oil heated for 20 min.)

| Clay, % | Crude oil (200° C.) | | | Alkali treated oil (100° C.) | | | Lecithin-free oil (100° C.) | | |
|---|---|---|---|---|---|---|---|---|---|
| | F.F.A., % | Rel. transmission | | F.F.A., % | Rel. transmission | | F.F.A., % | Rel. transmission | |
| | | 660 mμ | 440 mμ | | 660 mμ | 440 mμ | | 660 mμ | 440 mμ |
| 1 | 0.24 | 35.8 | 4.8 | 0.18 | 89.8 | 9.4 | 0.48 | 88.7 | 8.3 |
| 2 | 0.29 | 72.5 | 7.2 | 0.20 | 92.5 | 31.0 | 0.42 | 94.8 | 29.1 |
| 4 | 0.57 | 99.0 | 53.5 | 0.24 | 94.9 | 54.4 | 0.23 | 96.1 | 60.0 |
| 6 | 0.96 | 100.2 | 60.1 | 0.31 | 98.0 | 71.0 | 0.40 | 98.9 | 71.9 |
| 8 | 1.11 | 100.2 | 68.6 | 0.25 | 98.5 | 78.5 | 0.43 | 100.0 | 79.3 |
| 10 | 1.29 | 100.2 | 64.4 | 0.22 | 99.2 | 84.0 | 0.44 | 100.0 | 85.5 |
| 12 | 1.54 | 99.5 | 67.0 | 0.52 | 98.8 | 85.6 | 0.41 | 100.0 | 84.0 |

TABLE VIII

EFFECT OF SUPERFILTROL CONCENTRATION ON THE BLEACHING OF ALKALI TREATED MUSTARD OIL

(Heated for 20 min. at 100° C.)

| Clay concentration, % | F.F.A., % | Relative transmission | |
|---|---|---|---|
| | | 660 mμ | 440 mμ |
| 0* | 0.25 | 18.1 | 4.0 |
| 1 | 0.33 | 53.5 | 5.1 |
| 2 | 0.40 | 76.1 | 7.0 |
| 4 | 0.36 | 91.7 | 20.5 |
| 6 | 0.32 | 94.1 | 34.4 |
| 8 | 0.38 | 100.0 | 49.5 |
| 10 | 0.45 | 97.9 | 55.9 |
| 12 | 0.55 | 100.0 | 60.3 |

* *Alkali treated oil without any bleach.*

*Effects of Active Carbon, Added Water, and Modifications in Procedure*

It is apparent from Table X that active carbon was somewhat more effective when used along with Superfiltrol (Treatments 1 and 2), but reference to Table VII shows that 4% Superfiltrol alone yielded oil with approximately the same transmission.

Treatment 3 used a five minute heating period at 100° C. prior to addition of bleaching clay. The resulting oil had poorer transmission at 440 mμ than oil from ordinary bleaching (Table V). This suggests that readily volatilizable material did not affect the activity of the clay. The addition of 1 and 2% water (Treatments 4 and 5) showed no appreciable effect. Treatments 6 and 7 involved two 2% Superfiltrol bleachings of mustard oils. But results on comparable oils subjected to one 4% bleach (Tables VII and VIII)

indicate that the double procedure was slightly less effective than the simpler, single operation.

TABLE IX

EFFECT OF CONCENTRATION OF SUPERFILTROL ON THE BLEACHING OF FULLY ALKALI REFINED RAPE AND MUSTARD OILS

(Oil at 100° C. for 20 min.)

| Superfiltrol concentration, % | Rapeseed oil | | | Mustard seed oil | | |
|---|---|---|---|---|---|---|
| | F.F.A., % | Rel. transmission | | F.F.A., % | Rel. transmission | |
| | | 660 mμ | 440 mμ | | 660 mμ | 440 mμ |
| 0 | 0.068 | 72.5 | 5.0 | 0.069 | 52.0 | 6.0 |
| 1 | 0.066 | 100.0 | 57.8 | 0.053 | 90.5 | 9.0 |
| 2 | 0.037 | 100.0 | 78.0 | 0.064 | 97.0 | 33.0 |
| 4 | 0.042 | 100.0 | 91.0 | 0.045 | 100.0 | 54.5 |
| A.O.C.S.* 4% | 0.076 | 97.0 | 52.0 | 0.138 | 90.0 | 12.0 |
| 6 | 0.093 | 100.0 | 91.8 | 0.075 | 96.5 | 59.0 |
| 8 | 0.101 | 100.0 | 92.0 | 0.103 | 97.5 | 62.0 |
| 10 | 0.132 | 100.0 | 95.5 | 0.200 | 99.9 | 64.0 |
| 12 | 0.241 | 100.0 | 93.5 | 0.141 | 98.5 | 66.5 |

* *American Oil Chemists Society Standard Fuller's earth.*

TABLE X

MISCELLANEOUS BLEACHING EXPERIMENTS ON RAPESEED AND MUSTARD SEED OILS

| No. | Description of bleaching and oils used | F.F.A., % | Relative transmission | |
|---|---|---|---|---|
| | | | 660 mμ | 440 mμ |
| 1 | Alkali treated rapeseed oil bleached for 20 min. at 100° C. with 4% Superfiltrol and 1% Darco carbon. | 0.56 | 93.0 | 61.5 |
| 2 | Alkali treated rapeseed oil bleached for 20 min. at 100° C. with 4% Superfiltrol, filtered, and then subjected to a similar treatment with 1% Darco carbon. | 0.20 | 81.0 | 53.0 |
| 3 | Crude rapeseed oil heated for 5 min. at 100° C. then 4% Superfiltrol added and held at 100° C. for 20 min. | 0.29 | 90.0 | 7.5 |
| 4 | Crude rapeseed oil, 1% water added and then treated as above (3). | 0.26 | 91.5 | 14.1 |
| 5 | Crude rapeseed oil, 2% water added and then treated as above (3). | 0.25 | 95.2 | 8.0 |
| 6 | Crude mustard oil heated for 20 min. at 100° C. with 2% Superfiltrol added, filtered, and operation repeated with another 2% Superfiltrol. | 0.55 | 67.8 | 5.5 |
| 7 | Alkali treated mustard oil, and as in (6). | 0.27 | 85.4 | 19.8 |

*Effects of Oil Refining*

Neither crude mustard nor crude rapeseed oil showed satisfactory bleaching unless high percentages of clay were used in conjunction with temperatures substantially higher than 100° C. (Tables IV, V, VI, VII). Conversely, lecithin-free, alkali treated, or alkali refined oils bleached fairly effectively. However, conventional alkali refining yielded bleached oils with substantially better transmission for a given percentage of bleaching clay (Tables VII and IX).

*Changes in Transmission of Bleached Oil on Storage for Eight Weeks*

The data of Table XI give the relative transmissions of bleached rape and mustard oils as determined initially and after standing in the diffuse light of the laboratory for an eight week period. Aging tended to improve transmission slightly, lecithin-free rape oil showing somewhat greater change than either alkali treated rape or mustard oils.

TABLE XI

EFFECT OF EXPOSURE TO DIFFUSE LIGHT FOR EIGHT WEEKS ON RELATIVE LIGHT TRANSMISSION OF BLEACHED OILS

(Oils bleached for 20 min. at 100° C.)

| Description of oil | Superfiltrol, % | Relative transmission | | | |
|---|---|---|---|---|---|
| | | 660 mμ | | 440 mμ | |
| | | Initial | After eight weeks | Initial | After eight weeks |
| Lecithin-free rape | 1 | 88.7 | 97.2 | 8.3 | 10.5 |
| | 2 | 94.8 | 100.0 | 29.1 | 32.4 |
| | 4 | 96.1 | 100.0 | 60.0 | 64.8 |
| Alkali treated rape | 2 | 92.5 | 93.0 | 31.0 | 34.8 |
| | 6 | 98.0 | 99.5 | 71.0 | 75.5 |
| Alkali treated mustard | 2 | 76.1 | 80.0 | 7.0 | 8.0 |
| | 4 | 91.7 | 91.5 | 20.5 | 22.0 |
| | 6 | 94.1 | 96.5 | 34.4 | 37.0 |
| | 10 | 97.9 | 99.5 | 55.9 | 57.0 |

## Discussion

These results demonstrate that dark, unattractive erucic acid oils from commercial rapeseed or mustard seed screenings are readily amenable to bleaching. As little as 2% Superfiltrol bleaching clay decolorizes alkali refined oils and yields products similar in color to commercial salad oils, such as corn and cottonseed oils. While the most efficient bleaching was done on conventionally alkali refined material, both the lecithin-free and alkali treated oils yielded reasonably satisfactory products. Interest in these alternative refining procedures resulted from a study of German wartime practice (3).

Such modifications in refining may have a bearing on resistance to oxidation and flavor reversion, and may also provide less expensive procedures in the preparation of oils for industrial purposes.

Crude oils could be bleached with fairly good results at temperatures of the order of 200° C. (Table VII) but an appreciable increase in free fatty acid content occurred. German technology indicates that such oils with 2% or less free fatty acid content may be deslimed with spent bleaching clay, hydrogenated, and then alkali refined. Table V shows that fairly good bleaching of crude oil occurred with 4% bleaching clay and temperatures between 175° and 200° C. with only a comparatively slight increase in the free fatty acid content (0.6%). These results suggest the possibility of applying the German practice. It is possible that direct bleaching of these dark oils at a relatively high temperature may be an economic procedure preparatory to the preparation of sulphated, thermally polymerized, or other industrial oils.

## Acknowledgment

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# CANADIAN ERUCIC ACID OILS

## II. EDIBLE USE OF RAPE AND MUSTARD SEED OILS[1]

By H. J. Lips[2], N. H. Grace[2] and Elinor M. Hamilton[3]


### Abstract

Canadian grown rape and mustard seed oils were alkali refined with 10° Bé. sodium hydroxide, bleached for 20 min. at 212° F. with 2 or 4% Superfiltrol, and deodorized at 464° F. for one hour. These oils were lighter in color and more viscous than commercial corn oil, had smoke points over 400° F., and were clear at refrigerator temperature (40° F.). Consumer acceptance tests indicated that the erucic acid oils, either fresh or aged for 10 days at 100° F., were generally as acceptable as corn oil when used as salad oils or for the preparation of mayonnaise and pastry. The fresh oils were generally not as satisfactory as corn oil for the preparation of doughnuts, although some of the aged oils gave results comparable with those for aged corn oil.


### Introduction

The possibilities of Canadian-grown erucic acid oils as edible fat sources were suggested in an earlier publication (6). Cold pressed rape and mustard oils have relatively mild flavor and odor and have long been used for edible purposes, chiefly in the Orient and some European countries, but the hot pressed or solvent extracted oils have strong odor and flavor and are not palatable in the unprocessed state. Improved materials of the latter type have had little culinary application except in Germany (6), perhaps because of anticipation of difficulties with flavor reversion (3, p. 194).

The chief requirements for a good salad and cooking oil are: attractive color, agreeable "feel" or "texture" to the palate, bland or pleasing flavor, good keeping quality, high smoke point (preferably over 400° F.), and clarity at refrigerator temperature (40° F.). These points are considered in the present paper in regard to hot pressed, fully refined rape and mustard seed oils, as indications of their acceptability for food use.

### Materials and Methods

The crude rape and mustard seed oils used in this experiment were described in the first paper of the series (5). They were refined with 10° Bé. alkali, bleached with 2 or 4% Superfiltrol under carbon dioxide for 20 min. at 212° F., and steam deodorized under vacuum at 464° F. for one hour in the laboratory according to accepted processing methods (3). A special refined, 4% bleached rape oil was prepared by the use of water washing techniques, before and after refining, to remove phosphatides. This procedure was described in

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reports on the German fat industry as an effective means of eliminating flavor reversion (6). The resulting oil contained no detectable quantity of phosphorus and hence was termed "lecithin-free." Each test sample of processed erucic acid oil was a composite of either two or three batches individually prepared from the same source material. Commercially processed corn (salad) oil was used as a reference material in all tests, and comparisons were made on fresh oils and oils aged for 10 days at 100° F. None of the oils showed clouding or precipitation when held at 40° F.

Measurements of color (5), fluorescence (7), kinematic viscosity (2, p. 647), peroxide oxygen (4), free fatty acid (9), and smoke point (1) were made at different stages of processing and use.

Mayonnaise, pastry, and doughnuts were prepared according to the recipes given in Table I. Pastry was baked 10 min. at 435° F. and served at room temperature, and doughnuts were fried in the oils at 355° to 365° F. for three minutes and served warm.

TABLE I

RECIPES FOR VEGETABLE OIL PRODUCTS, GIVEN IN GRAMS

| Constituent | Product | | |
|---|---|---|---|
| | Mayonnaise | Pastry | Doughnuts |
| Eggs | — | — | 96 |
| Egg yolk | 18 | — | — |
| Flour | — | 112 | 500 |
| Sugar | 2½ | — | 200 |
| Oil | 200 | 50 | — |
| Shortening | — | — | 25 |
| Milk | — | — | 244 |
| Water | 15 | 15-20 | — |
| Baking powder | — | — | 15 |
| Cinnamon | — | — | ½ |
| Mustard | ½ | — | — |
| Nutmeg | — | — | ½ |
| Paprika | Trace | — | — |
| Pepper | Trace | — | — |
| Salt | 1 | 2 | 4 |
| Vinegar | 15 | — | — |

The oils and prepared products were scored by a 24-member panel (8); zero represented the ideal in the estimation of the scorer, and excess or deficiency of the property under study was rated on an integral scale of + 5 to − 5. A score numerically greater than ± 2.5 units indicated a definitely unacceptable product. The oils and mayonnaises were rated for color, texture, odor, and flavor, but the pastries and doughnuts were rated for odor and flavor only. All organoleptic data were examined statistically by means of analyses of variance.

## Results

Physical and chemical measurements for the corn, mustard, and rapeseed oils at various stages of processing and use are given in Table II. Tables III and IV show organoleptic data for the oils and for mayonnaise, pastry, and doughnuts prepared with them.

TABLE II

CHEMICAL AND PHYSICAL MEASUREMENTS ON VEGETABLE OILS AT VARIOUS STAGES OF PROCESSING AND USE

| Oil | Condition of oil | | | | |
|---|---|---|---|---|---|
| | 1 Bleached | 2 Bleached and deodorized | 3 Bleached, deodorized, and aged | 4 As in column 2, fried | 5 As in column 3, fried |
| | Measurement | | | | |
| | *A. Transmission, %, at 440 mμ relative to mineral oil (Stanolax)* | | | | |
| Corn* | — | 32 | 25 | 28 | 27 |
| Mustard, 2% bleach | 38 | 58 | 51 | 43 | 43 |
| Mustard, 4% bleach | 50 | 62 | 54 | 44 | 43 |
| Rape, 2% bleach | 75 | 93 | 84 | 64 | 60 |
| Rape, 4% bleach | 85 | 89 | 87 | 62 | 59 |
| Rape, "lecithin-free" | 82 | 87 | 84 | — | 57 |
| | *B. Fluorescence, Coleman photofluorometer units, 1 gm. of oil in 100 ml. xylol, corrected for fluorescence of xylol* | | | | |
| Corn* | — | 71 | 67 | 50 | 49 |
| Mustard, 2% bleach | 70 | 58 | 57 | 50 | 49 |
| Mustard, 4% bleach | 68 | 56 | 57 | 58 | 47 |
| Rape, 2% bleach | 11 | 2 | 6 | 10 | 11 |
| Rape, 4% bleach | 3 | 2 | 2 | 10 | 12 |
| Rape, "lecithin-free" | 16 | 12 | 11 | — | 17 |
| | *C. Viscosity, centistokes at 100° F.* | | | | |
| Corn* | — | 33.6 | 33.5 | 35.7 | 34.7 |
| Mustard, 2% bleach | 41.6 | 42.3 | 42.3 | 44.6 | 44.9 |
| Mustard, 4% bleach | 41.9 | 42.3 | 42.5 | 44.4 | 44.4 |
| Rape, 2% bleach | 46.5 | 47.4 | 47.6 | 48.9 | 49.5 |
| Rape, 4% bleach | 46.7 | 46.8 | 46.8 | 48.3 | 49.1 |
| Rape, "lecithin-free" | 46.8 | 47.6 | 47.6 | — | 49.8 |
| | *D. Peroxide value, ml. of 0.002 N thiosulphate per gm.* | | | | |
| Corn* | — | 0.0 | 0.0 | 3.9 | 4.5 |
| Mustard, 2% bleach | 0.0 | 0.0 | 0.0 | 4.9 | 5.4 |
| Mustard, 4% bleach | 0.0 | 0.0 | 4.0 | 4.3 | 4.6 |
| Rape, 2% bleach | 0.0 | 0.0 | 2.6 | 4.5 | 4.7 |
| Rape, 4% bleach | 0.0 | 0.0 | 6.0 | 4.0 | 4.6 |
| Rape, "lecithin-free" | 0.0 | 0.0 | 6.2 | — | 6.1 |

** The corn oil was used as purchased and received no further processing. Column 2 gives values for the untreated corn oil and Column 3 for the untreated, aged corn oil.*

TABLE II—*Concluded*

CHEMICAL AND PHYSICAL MEASUREMENTS ON VEGETABLE OILS AT VARIOUS STAGES OF PROCESSING AND USE—*Concluded*

| Oil | Condition of oil | | | | |
|---|---|---|---|---|---|
| | 1 Bleached | 2 Bleached and deodorized | 3 Bleached, deodorized, and aged | 4 As in column 2, fried | 5 As in column 3, fried |
| | Measurement | | | | |
| | *E. Free fatty acid content, as % oleic acid* | | | | |
| Corn* | — | — | — | 0.1 | 0.1 |
| Mustard, 2% bleach | — | — | — | 0.1 | 0.2 |
| Mustard, 4% bleach | — | — | — | 0.2 | 0.2 |
| Rape, 2% bleach | — | — | — | 0.1 | 0.2 |
| Rape, 4% bleach | — | — | — | 0.2 | 0.2 |
| Rape, "lecithin-free" | — | — | — | — | 0.2 |
| | *F. Smoke point, ° F.* | | | | |
| Corn* | — | 445 | — | — | — |
| Mustard, 2% bleach | — | 405 | — | — | — |
| Mustard, 4% bleach | — | 405 | — | — | — |
| Rape, 2% bleach | — | 420 | — | — | — |
| Rape, 4% bleach | — | 425 | — | — | — |

* *The corn oil was used as purchased and received no further processing. Column 2 gives values for the untreated corn oil and Column 3 for the untreated, aged corn oil.*

TABLE III

DIFFERENCES IN ORGANOLEPTIC RATINGS FOR VEGETABLE OILS AND THEIR PRODUCTS

| Material | Texture | Color | Odor | Flavor |
|---|---|---|---|---|
| Oils | o | ** | o | ** |
| Mayonnaise | o | ** | o | o |
| Pastry | — | — | o | ** |
| Doughnuts | — | — | ** | ** |

o *Indicates no significant differences found.*

** *Indicates highly significant differences (1% level); these differences are shown in detail in Table IV.*

The three oils exhibited differences in both experimental measurements and organoleptic ratings. The relative light transmission of the oils at 440 mμ increased considerably in the order: corn, mustard, and rape (Table II), and the scoring panel was able to detect significant differences in color of oils and mayonnaises (Table III). Relative transmissions for the oils at 660 mμ were all in the range 97 to 100%, so these are not reported. Although mustard oil appeared to be the most fluorescent in daylight, corn oil had the greatest fluorescence in ultraviolet light (375 mμ) with mustard intermediate, and rape least. "Lecithin-free" rape was more fluorescent in ultraviolet light

TABLE IV

ORGANOLEPTIC RATINGS FOR VEGETABLE OILS AND THEIR PRODUCTS FOR THOSE ATTRIBUTES THAT SHOWED SIGNIFICANT DIFFERENCES

| | Oil | | | | Mayonnaise | | Pastry | | Doughnuts | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Color | | Flavor | | Color | | Flavor | | Odor | | Flavor | |
| | Fresh | Aged | Fresh | Aged | Fresh | Aged | Fresh | Aged | Fresh | Aged | Fresh | Aged |
| Corn oil | +0.8 | +1.0 | +0.9 | +0.1 | +0.3 | +0.1 | +1.2 | +0.3 | +0.1 | +0.3 | +0.1 | +0.5 |
| Mustard, 2% bleach | −0.2 | +0.1 | +0.1 | +0.1 | −0.6 | −0.1 | +0.9 | +0.7 | +0.8 | +0.6 | +1.4 | +1.0 |
| Mustard, 4% bleach | −0.4 | −0.1 | −0.3 | +0.8 | −0.1 | −0.5 | +0.6 | +1.4 | +1.4 | +0.8 | +1.5 | +0.8 |
| Rape, 2% bleach | −1.6 | −1.7 | −0.5 | 0.0 | −0.3 | −0.6 | +1.0 | +0.5 | +0.4 | +0.4 | +0.9 | +0.4 |
| Rape, 4% bleach | −1.4 | −2.0 | −0.1 | +1.0 | −0.6 | −0.7 | +0.7 | +1.1 | +0.5 | +1.6 | +1.0 | +2.3 |
| Rape, "lecithin-free" | | −1.7 | | −0.3 | | −0.9 | | +1.6 | | +0.5 | | +0.6 |
| Necessary difference (5% level) | ±0.5 | | ±0.6 | | ±0.4 | | ±0.5 | | ±0.4 | | ±0.5 | |

than the other rape oils. Corn, mustard, and rape oils showed increasing viscosity in that sequence, but the panel was unable to detect significant differences in texture of oils or mayonnaises. All initial peroxide values were nil; free fatty acid content of oils after use for frying doughnuts was uniformly small; and smoke points were high, with a slight increase from mustard to rape to corn oil. In spite of the apparent similarity in quality, as assessed by these objective methods, the scoring panel was able to detect significant differences in flavor and odor in some of the products (Table III).

The characteristics of the oils were altered by processing, aging, and frying (Table II). Deodorization generally reduced color and fluorescence but increased viscosity slightly; aging intensified color, had little effect on fluorescence, and none on viscosity; frying increased color and viscosity, decreased fluorescence for corn and mustard, and increased fluorescence for rape oil. Peroxide values of aged and fried oils remained quite low; corn and the 2% bleached erucic acid oils showed the least change.

As shown in Table IV, corn oil was considered too dark and rape oil too light, with mustard approaching the ideal. For mayonnaise, color differences were smaller, and only the rape oil products were thought to be deficient in this respect. Flavor scores for the oils deviated significantly from the nil value for fresh corn oil; and for aged, 4% bleached rape and mustard oils. Pastry and doughnut mean scores were all positive, indicating degrees of excess flavor and odor attributable to the oils used. The erucic acid oils were not as satisfactory as corn oil for the preparation of doughnuts, although some of the aged oils gave reasonably satisfactory results.

The relatively poor flavor scores for fresh corn oil and for pastry prepared with it indicated that the natural flavor of the oil was considered too strong by some of the tasters. This flavor was evidently diminished or obscured by aging and baking or frying. The apparent improvement on aging of some of

the other oils used in the preparation of pastry and doughnuts may have been due to partial volatilization or breakdown of products of aging when the oils were subjected to baking or frying conditions (3, p. 290).

When processing steps are considered in conjunction with experimental results for the single samples used here (Tables II and IV), it would appear that increasing the bleach for rape and mustard oils from 2 to 4% was not advantageous. There was no important decrease in color and more peroxide was formed on storage in the 4% bleached oils. The specially treated "lecithin-free" rape oil (4% bleach) did not show any superiority in organoleptic scores as compared to 2% bleached rape, but was generally better than 4% bleached rape.

Erucic acid oils have hitherto been used for industrial purposes in Canada. These preliminary results indicate that they also merit serious consideration as possible sources of edible materials.

## Acknowledgments

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# THE OXIDATION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

## VI. THE PREVENTION OF PRE-IGNITION AND DETONATION IN GAS ENGINES[1]

By R. O. King[2], W. A. Wallace[3] and B. Mahapatra[4]


### Abstract

The experiments described show that town gas containing hydrogen in large concentration can be used as fuel for a carburetor type Otto cycle engine at compression ratios rising to 10 : 1 and in mixtures with air in any proportion, if the accumulation of fluffy carbon in the combustion space be prevented. The carbon is produced mainly by pyrolysis of the lubricating oil. Confirmation of the nuclear theory of ignition, advanced in Part IV to explain the cause of detonation in engines, is thus obtained. Performance data are given for the variation of power and economy with mixture strength and ignition timing at compression ratios of 6, 8, and 10 : 1.


### Introduction

It has long been known that the power and efficiency of gas engines have been limited by the necessity of using relatively weak gas–air mixtures and low compression ratios in order to avoid pre-ignition and detonation. Both effects are commonly believed to be due to ignition of the combustible mixture by sudden compression and/or by hot surfaces in the combustion space. Both increase in severity with increase in the proportion of hydrogen in the gas.

The severity of the effects mentioned has been mitigated by reducing the inflammability of the combustible mixture or by cooling the more highly heated surfaces of the combustion space. Thus, Dugald Clerk (1) added cooled exhaust gases to the entering mixture; Bertram Hopkinson (4) provided a water sprinkler system in the combustion space and a modification of the system was used in the Crossley Gas Engine (2, p. 39). The Koerting Gas Engine (German) was fitted with a separate water cooled body in the combustion space (2, p. 95). Recent developments aimed to avoid pre-ignition and detonation are the high compression gas engine and the Dual Fuel engine using gas and injected oil. Both operate at Diesel engine compression ratios. High pressure gas is injected late in the compression stroke in the first mentioned type (Walter (9) and Erren (3) ) and ignition is by electric spark. Ignition is by injected oil in the Dual Fuel type as in the compression ignition engine, and mixing of the gas with air does not occur until the inlet valve opens (Jones (5, p. 37) ).

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*Contribution by the Defence Research Board (Canada) and the Department of Mechanical Engineering, University of Toronto.*

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[4] *Overseas Scholar, Government of India.*

The above mentioned methods of increasing the power and economy of gas engines are based on the theory that pre-ignition and detonation are inherent in the nature of the gas, especially of the hydrogen constituent. It is shown, however, by the experiments described in Part V (8) that the pre-ignition and detonation observed when hydrogen–air mixtures are used in an engine are due to the igniting effect of finely divided carbon derived from pyrolysis of the lubricating oil.

Commercial fuel gases, even if composed mainly of hydrogen and carbon monoxide, usually contain some proportion of hydrocarbon which by pyrolysis at end gas temperatures might yield finely divided carbon in sufficient concentration to cause ignition and consequent detonation (Part IV (7) ). The lubricating oil would otherwise be the sole source of carbon, as when using hydrogen.

It became of interest, therefore, to determine if pre-ignition and detonation in engines using fuel gas could be avoided, as in the hydrogen engine, by preventing the accumulation of finely divided carbon in the combustion space. Experiments made accordingly are described in this Part and show that the gas, pre-mixed with air in any proportion, can be used at compression ratios rising to 10 : 1, the limit of the variable compression C.F.R. engine, without pre-ignition or detonation and with a consequent increase in power and economy.

## Experimental

The C.F.R. knock testing engine in the Department of Mechanical Engineering, University of Toronto, was used for the experiments with Toronto town gas as the fuel. The special features of the engine are described in Part V (8).

*The Fuel Gas*

The composition and calorific value of Toronto town gas are checked continuously by the Consumers Gas Company. The composition at the time of the experiments was as below, in percentage volumes.

| | | | |
|---|---|---|---|
| Hydrogen | 49.1 | Ethane | 2.3 |
| Carbon monoxide | 19.1 | Nitrogen | 7.8 |
| Methane | 12.9 | Carbon dioxide | 3.7 |
| Heavy hydrocarbons | 4.3 | Oxygen | 0.8 |

The calorific value was 475 B.t.u. per cu. ft. at 60° F. and 30 in. of mercury barometric pressure, when saturated with water vapor. Temperature at time of use was 78.5° F. and pressure 29.9 in. of mercury, the calorific value being then,—

$$475 \times \frac{520}{538.5} \times \frac{29.9}{30} = 459 \text{ B.t.u.}$$

The gas was supplied to the engine by using the device illustrated in Fig. 1, the standard diffuser being removed from the throat of the carburetor venturi.

The C.F.R. carburetor was otherwise intact and a change to liquid fuel could be made when required.

The rate of gas supply to the engine was measured by a new and freshly calibrated No. 1A Sprague meter.

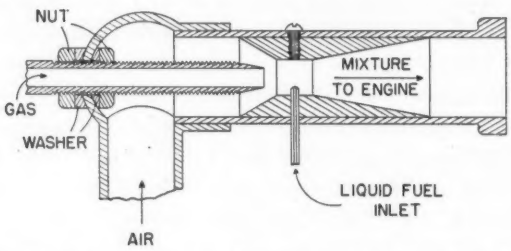


FIG. 1. *Carburetor arrangement used for running the C.F.R. engine on town gas.*

*Experimental Procedure and Conditions*

The engine had been run on hydrogen prior to the experiments with town gas and the routine cleaning method then adopted, Part V (8), to prevent the accumulation of fluffy carbon in the combustion space was continued. The engine was always run at 900 r.p.m. The jacket water temperature was maintained at 212° F. by the C.F.R. standard method of evaporative cooling, using distilled water.

The rate of flame propagation in town gas – air mixtures is so much slower than in hydrogen–air mixtures and varies so much with mixture strength that maximum power for a particular compression ratio and mixture strength is obtained only if a particular ignition timing is used. It was decided, therefore, to run series of experiments at compression ratios of 6, 8, and 10 : 1 to determine the ignition timing required for maximum power when using a series of mixture strengths varying from very weak to very rich. Families of graphs were thus obtained relating maximum power to ignition timing and mixture strength at the three values of the compression ratio.

*Experimental Results*

The combined effect of mixture strength and ignition timing on power output when the compression ratio was 6 : 1 is shown by the graphs of Fig. 2. Similar families of graphs were obtained for compression ratios of 8 and 10 : 1, but are not reproduced.

The graphs of Fig. 3 then give the relation between power output and mixture strength when the optimum ignition timing is used for every experimental point; the timing in degrees advance being given by the figures in circles.

The engine ran smoothly without combustion noise even at the maximum available compression ratio of 10 : 1, and when using the mixture strength and spark advance giving maximum power.

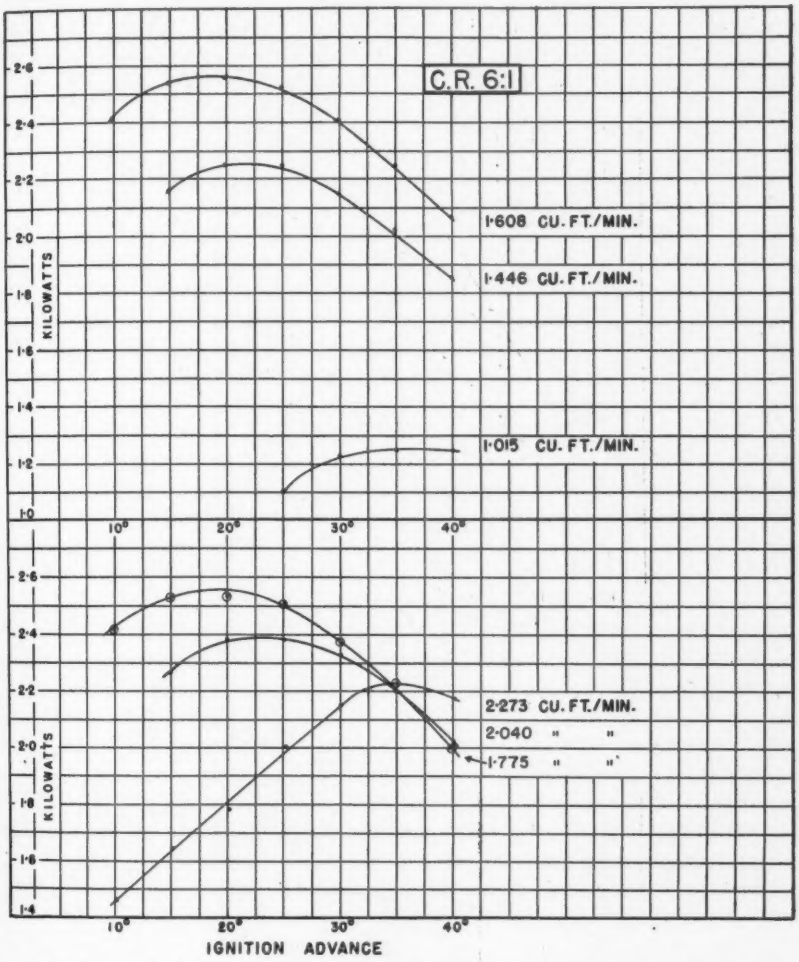


FIG. 2. *Effect of mixture strength and ignition advance on power output when using town gas as fuel for the C.F.R. engine, running at 900 r.p.m., compression ratio 6 : 1.*

Indicated thermal efficiencies and indicated mean effective pressures calculated from the graphs of Fig. 3 are given in Tables I, II, and III for compression ratios of 6, 8, and 10 : 1, respectively, and for varying mixture strengths. The percentages of mixture strength are in respect of the rate of gas supply required for maximum power, and it will be seen by reference to the graphs of Fig. 3 that this rate varies with compression ratio.

The values for indicated horse power given in the tables were obtained by the usual motor method. The power loss obtained accordingly is added to the net power output. The losses in the C.F.R. unit used for the experiments

are large because they include the electrical and mechanical losses in both the main and auxiliary generators in addition to the pumping and mechanical losses in the engine which could not be measured separately because the engine

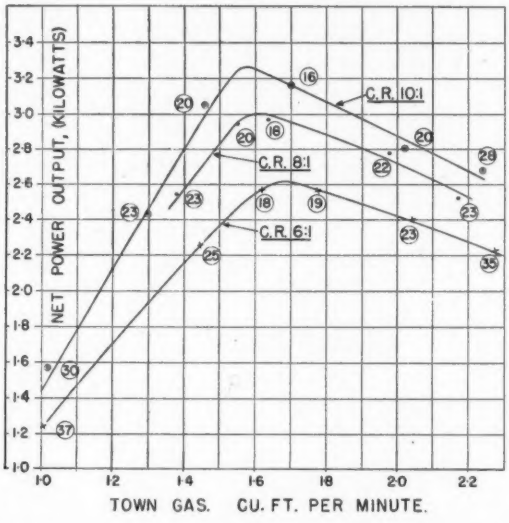


FIG. 3. *Relation between power output and mixture strength at compression ratios of 6, 8, and 10 : 1, with optimum ignition advance as shown by figures in circles, C.F.R. engine running on town gas at 900 r.p.m.*

TABLE I

COMPRESSION RATIO 6 : 1

| Gas – air mixture | Cu. ft. gas/min. | I.H.P. | Indicated thermal efficiency | I.M.E.P., lb./sq. in. |
|---|---|---|---|---|
| 30% weak | 1.17 | 4.20 | 0.33 | 98 |
| 20% weak | 1.34 | 4.70 | 0.32½ | 110 |
| 10% weak | 1.51 | 5.19 | 0.32 | 121 |
| Max. power | 1.68 | 5.51 | 0.30 | 129 |
| 10% rich | 1.85 | 5.37 | 0.28 | 126 |
| 20% rich | 2.02 | 5.24 | 0.25 | 122 |
| 30% rich | 2.18 | 5.05 | 0.22 | 118 |

was not fitted with a swinging field electrical dynamometer. The total losses measured after the engine had been raised to working temperature by running on benzene were, in kilowatts, 1.61 at 10 : 1 C.R.; 1.59 at 8 : 1 C.R.; 1.48 at 6 : 1 C.R.

The cylinder diameter of the engine is 3.25 in., the stroke is 4.5 in. and as the trials were run at 900 r.p.m., indicated mean effective pressure (I.M.E.P.) in pounds per square inch,

$$= \text{Indicated horsepower} \times 23.41 .$$

TABLE II

COMPRESSION RATIO 8 : 1

| Gas – air mixture | Cu. ft. gas/min. | I.H.P. | Indicated thermal efficiency | I.M.E.P., lb./sq. in. |
|---|---|---|---|---|
| 15% weak | 1.37 | 5.48 | 0.37 | 128 |
| 10% weak | 1.50 | 5.94 | 0.37 | 139 |
| Max. power | 1.61 | 6.15 | 0.36 | 144 |
| 10% rich | 1.77 | 6.02 | 0.32 | 141 |
| 20% rich | 1.93 | 5.86 | 0.28 | 137 |
| 30% rich | 2.09 | 5.67 | 0.25 | 133 |

TABLE III

COMPRESSION RATIO 10 : 1

| Gas – air mixture | Cu. ft. gas/min. | I.H.P. | Indicated thermal efficiency | I.M.E.P., lb./sq. in. |
|---|---|---|---|---|
| 30% weak | 1.10 | 4.54 | 0.38 | 106 |
| 20% weak | 1.25 | 5.24 | 0.39 | 122 |
| 10% weak | 1.41 | 5.95 | 0.39 | 139 |
| Max. power | 1.57 | 6.53 | 0.38 | 153 |
| 10% rich | 1.73 | 6.36 | 0.34 | 149 |
| 20% rich | 1.88 | 6.18 | 0.30 | 145 |
| 30% rich | 2.04 | 5.96 | 0.27 | 139 |

Taking the calorific value* of the gas in British thermal units and using f.p.s. units, the indicated thermal efficiency,

$$= \frac{\text{Indicated hp.} \times 33000}{\text{Cu. ft. gas per min.} \times \text{calorific value} \times 778}$$

## Discussion of Experimental Results

The primary object of the experiments was to test the validity of the nuclear theory of ignition advanced in Part IV (7) as a working hypothesis for investigations of combustion as it occurs in engines. The results confirm the theory in that ignition of town gas–air mixtures was not obtained by nearly adiabatic compression in a combustion space maintained at 212° F. and containing a hot exhaust valve, compression ratio being 10 : 1, if the concentration of nuclei of ignition, as finely divided carbon, was maintained at a relatively low value.

The experiments considered as engine trials to determine power and efficiency are regarded as of a preliminary nature. Measurements were, however, made with the degree of accuracy usually employed in engine trials and the values obtained for indicated thermal efficiency and indicated mean effective pressure, as given in Tables I, II, and III, are of interest.

* *The "higher" calorific value of 459 B.t.u. per cubic foot was used in the calculations.*

*Indicated Thermal Efficiency*

It is generally considered that thermal efficiency increases substantially on going to weak mixtures. This characteristic is shown by the increase of 10% for 6 : 1 compression ratio, Table I, but referring to Tables II and III it will be noted that thermal efficiency tends to become constant on the weak side of maximum power mixture strength, as the compression ratio is increased; furthermore the mixture strength required for maximum power diminishes appreciably as the compression ratio is raised. Both effects may be due to the ignition advance for maximum power at any mixture strength, diminishing as compression ratio is raised as shown by the figures in circles, Fig. 3. Heat of combustion would be added more nearly at constant volume with decrease in ignition advance, and, the combustion period being shortened accordingly, less heat would be lost to the cool surfaces of the combustion chamber. Thus when hydrogen was used in the engine and ignition advance was zero or even −5°, the maximum thermal efficiency obtained, Part V (8), was 0.42 as compared with 0.39 for town gas, or 70% and 65%, respectively, of the air standard efficiency of 0.598 at 10 : 1 compression ratio.

*Mean Effective Pressure*

A maximum of 153 lb. per sq. in. was obtained for indicated mean effective pressure at 10 : 1 compression ratio (see Table III). The mechanical efficiency of the C.F.R. engine used for the experiments could not be measured but is known to vary from 85% to 88% in engines of the type. Assuming the lower value, 130 lb. per sq. in. is obtained for the brake mean effective pressure. According to Kent (6, p. 1236) it is necessary to limit B.M.E.P. in ordinary gas engines to 65 lb. per sq. in. to avoid pre-ignition and detonation, especially when using coke oven or illuminating gas; both these gases and Toronto town gas contain hydrogen in similar large proportion. The limitation has been shown to be unnecessary if nuclear ignition be avoided, and it is of interest to compare the performance of the C.F.R. engine obtained accordingly with that of the 'National' gas engine in the Heat Engine Laboratory, University of Toronto. The relevant data are given in Table IV.

TABLE IV

FULL POWER PERFORMANCE DATA, C.F.R. AND 'NATIONAL' GAS ENGINES, ON TOWN GAS

| Engine | R.p.m. | Gas per I.H.P./hr., cu. ft. | Compression ratio | I.M.E.P., lb./sq. in. | Indicated thermal efficiency |
|---|---|---|---|---|---|
| C.F.R. | 900 | 14.4 | 10 : 1 | 153 | 0.38 |
| National | 180 | 18.9 | 4.85 : 1 | 95 | 0.28 |

The higher mean effective pressure and speed of the C.F.R. have a favorable effect on power-to-weight ratio. Thus, I.H.P. of the C.F.R. is 17.5 per 100 cu. in. of piston displacement, whereas the similar figure for the National engine is 2.17 only.

### *Conclusion*

The experiments show that on preventing nuclear ignition of the gas–air mixture it becomes possible to operate the C.F.R. engine at any desired compression ratio while using mixture strengths varying from very weak to very rich and to obtain corresponding power and economy. The engine was run without throttle control, and, by using a relatively high compression ratio, 10 : 1 for example, power output could be varied over a wide range by controlling the rate of gas supply.

## Acknowledgments

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# CORROSION OF A STEEL SHIP IN SEA WATER[1]

By K. N. Barnard[2]

## Abstract

The corrosion of a steel ship in sea water has been investigated by studying the electrical potentials in the sea close to the hull. The surveys were made in conjunction with a drydocking program during which the state of the hull was deliberately altered so that the corrosion patterns could be followed under a variety of hull conditions, and were supplemented by visual inspections of the ship when in drydock. Typical results are described and discussed. Some failures of the present anticorrosive technique are indicated and some possible remedies suggested.

## Introduction

Until recent years the corrosion of the underwater hulls of steel ships in sea water was generally accepted to be a necessary evil. The main efforts to mitigate its effects centered around a 'rule of thumb' selection of coatings to protect the major part of the hull, and the use of zinc anodes placed near nonferrous metals to protect the adjacent steel. With the advent of the thin steel hulled minor war vessels up to and including the destroyer class, the corrosion problem became more serious. This stimulated interest in the subject, but attention was given to the development of better types of coatings rather than to the fundamentals of corrosion phenomena.

In general, work on the problem has been confined either to experiments on models or to making visual inspections of ships in drydock. In model research the various causes of corrosion are usually studied separately. No attempts are made to integrate the results experimentally on a small replica of a ship, including its many anomalies. Even if this were attempted, the results extrapolated to full scale could be misleading. For example, little difference in actual size would be expected for an incipient pit whether on a model or on a ship. Yet, because of the vastly different scale, the relative effect of the pit on the model would be exaggerated. If corrosion of a ship is studied by visual inspections alone, a considerable period may be required before changes become apparent, and many of the contributing factors cannot be observed in detail. Hence any comprehensive program aimed at reducing corrosion becomes a very long term project in which a number of ships are treated in different ways and usually examined only at the time of their scheduled refit. Statistical analysis is then applied to the observations, often taken by different personnel.

Naval Research Establishment at Halifax has for some time been carrying out experimental work on hull corrosion, some of which is described in this paper. To gain more direct information, a different method of full scale investigations was adopted, supplemented by visual inspections and model

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experiments. A number of preliminary trials showed that the general corrosion patterns occurring on ships could be satisfactorily located by measuring the electrical potentials found in the sea in the immediate vicinity of the subject vessel. These trials, which were taken on ships at rest, also indicated the desirability of more closely controlled conditions to determine the relative importance of various factors affecting hull corrosion.

In view of this, further trials were carried out over a period of nine months on a steel minesweeper. During this time a drydocking and hull treatment program was followed that allowed the surveys to be made under a variety of hull conditions. Surveys were made after each treatment at frequent intervals, until approximately steady state had been reached.

This report describes the technique and apparatus used; notes some of the advantages and limitations of the method; reviews the causes of cathodic areas; gives a brief history of the ship; outlines the drydocking hull treatment; presents an interpretation of the results of typical surveys, together with a description of pertinent circumstances; and offers a general discussion of the results with a view to possible improvements in the anticorrosion practice for ships.

## Surveying Technique and Apparatus

For a steel ship the ohmic resistance of the metallic hull is small compared to that of the sea path and contact resistance between the hull and sea. Thus the potential differences due to the current flow from anodic (corroding) regions of a ship to cathodic regions are greater in the sea than in the metallic circuit.

The potentials in the sea were measured using probe electrodes connected to a distant reference electrode through a millivoltmeter. By surveying over a grid system with the probe electrodes held close to the hull, the approximate positions of the anodic and cathodic regions were determined, and by inference the corroding regions of the hull ascertained.

The search electrodes were made by dipping silver gauze (2 by 6 in.), flame welded without flux to a silver wire, into fused silver chloride which was later reduced to silver – silver chloride by electrolysis. They were mounted concentrically on eight-conductor cable at 4 ft. intervals, one electrode per conductor. Each electrode was lagged with glass wool to reduce water motion at the electrode surface. Phenolite casings were used to protect the electrodes from damage and to allow them to slide easily around the ship's bilge keels. The cable was lead loaded and steel strengthened, and had sufficient negative buoyancy to hang in a vertical plane when held slack. The cable was marked every 4 ft. for 36 ft. on either side of the electrodes to aid in the determination of the athwartship positions of the electrodes.

The reference electrode was also a fused silver – silver chloride electrode. It was connected to a single conductor cabtire cable about 350 ft. long. The electrode was held about 60 ft. below the sea surface and was kept away from

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the ship by means of floats attached to the cable. The floats usually took the electrode out a distance from 150 to 250 ft, dependent on wind and tide.

To reduce the reading time, a millivoltmeter was used rather than a potentiometer to measure the potential of the search electrodes with respect to the reference electrodes. A suitable switching arrangement connected each of the eight electrodes in turn to the meter. A microammeter (Weston Model 490) with series resistances plus a switch for sensitivity control was used as the millivoltmeter. (The sensitivities were 0.2, 0.5, 1, 2, and 5 mv. per division, the added series resistance being 510, 1,540, 3,260, 6,620, and 16,870 ohms, respectively.) The 1 mv. per division setting was the normal sensitivity used, read to the closest half division. A 200 ft. length of light eight-conductor cable was used as a running lead between instrument station and search electrodes.

The surveys were conducted in Bedford Basin, a region free from industrial disturbances. With H.M.C.S. *Quinte*, which usually was not heavily loaded, it was found preferable to secure the ship by the stern to the buoy. This practice was standard from April 9 on. When the ship was secured by the bow even light winds tended to make it yaw severely, whereas when secured by the stern it kept a very steady position even in heavy winds. To prevent metallic contact between the ship and buoy, rope hawsers were used. The reference electrode was streamed from the bow when the ship was secured at the stern.

The electrode string was hauled taut at each station. The span was 28 ft. To obtain survey readings on a 4 ft. grid, the potentials were measured every 4 ft. along one side, holding say No. 1 search electrode 6 in. below the water line and returning along the other side with No. 8 electrode 6 in. below. This gave some useful overlapping of readings. The athwartship girth of the ship at the station and the distance of the far electrode from the water line were found from the position of the marker nearest the water line. Distances to the stations were measured from the bow. The longitudinal positioning of the electrodes was aided by the presence of vertical rivet lines occurring every 2 ft.

The potential of each search electrode with respect to the reference electrode was measured prior to and after each survey. These zero readings were taken with the electrodes hung from the stern of a wooden harbor craft about 500 ft. from the ship. The electrodes for these readings were kept at an average depth of about 45 ft., to avoid any possible effect caused by the presence of the harbor craft. To minimize extraneous effects, such as air exposure, the electrodes were towed in the water after the initial, and before the final, zero readings. The average value of an electrode's initial and final zero readings was used to correct the survey potential readings of the electrode. The electrodes were left in the sea between successive surveys with all the electrodes shorted, including the reference electrode. The short was removed about two hours before the initial zeros were taken.

When a survey was completed the ship returned to its jetty berth, where it was subjected to continual damage of the paint film at the water line by the jetty fenders. It did, however, make the occasional very short trip to sea.

## Plotting

The following method was selected to give a graphical representation of the results of these surveys. The keel line was drawn on cross-section paper and divided into stations corresponding in number to those marked on *Quinte*. At each station a distance corresponding to half the athwartship girth (as obtained during the survey) was marked on either side and at right angles to the keel line. These athwartship marks when joined represented the water line of the underwater girth of the ship measured along the electrode cable position, i.e., the approximate outline of the expanded underwater portion of the hull. The port side of the outline was indicated on the diagram. At each station the athwartship positions of the eight electrodes were marked in with respect to this outline. Points where readings were taken when the electrode cable was moved from stern to bow were marked with a tick ($\surd$) and the appropriate potential marked aft of the tick. A reading taken when the cable was moved from bow to stern was marked forward of a cross (+). The times that the readings were begun and ended on each side were indicated on the figures. The number of days after drydocking may be obtained from the date indicated.

The potential readings were changed to millivolts and corrected for zero out of balance before plotting. In contouring, the interval was not uniform or always the same for each figure, but depended on the general value of the intensities obtained for a given survey. The positive contours were drawn in full lines, negative contours dotted, and the zero contours in broken lines. No allowance was made for the varying distances of the electrodes from the hull, at projecting and re-entrant positions of the hull.

As an aid to the interpretation of results, the approximate positions of the outlets and underwater fittings with respect to the keel line have been drawn on the skeleton expanded diagram shown in Fig. 1.

## Advantages and Limitations of Method

*Advantages*

The advantages of this method of investigation were as follows. (*a*) The potential surveys were carried out at frequent time intervals, thus following the time changes of corrosion in some detail – without disturbing the process of corrosion. (*b*) The research was done under practical conditions but avoided frequent (and expensive) drydocking inspections. (*c*) Information was obtained regarding the relative importance of the various cathodic regions existing on the hull under varied conditions. This information cannot be secured from visual inspection of the ship in drydock. (*d*) Objective, quantitative results, more impartial than the subjective results of visual inspection, were obtained. (*e*) Better control was exercised in that, in some instances,

a given factor could be changed as soon as the surveys indicated that its influence had reached an approximately steady state. Thus the time needed for a given treatment was much shorter than would have been the case had drydocking inspection been the only criterion.

*Limitations*

The surveys were potential, not current density, surveys. Therefore it was not possible to calculate the amount of anodic material entering solution, nor always to rigorously separate anodic from cathodic regions. Consideration had to be given to several factors when interpreting results, particularly when the distance between anode and cathode was relatively short.

The manner in which the potentials were measured should be noted, especially in regard to the zero potential or reference potential. Theoretically the zero potential at a point was taken to be the potential that would be obtained in the absence of the ship. In practice the potentials were taken with reference to that of the sea some distance away from the ship.

The position of the zero equipotential contours for the case of multiple anodes and cathodes distributed at random would depend on the current flow from and to the individual anodes and cathodes. This current flow would be affected by the size, shape, and relative positions of anodes and cathodes, as well as by the presence of polarization and of corrosion deposits. Thus shifts in the zero equipotential positions are to be expected for a ship that had not only multiple anodic sources of the same type (e.g., zinc) but had a steel hull that could be either an anode or a cathode (or both), depending on the condition of its paint and on the activity of its zincs and propellers, all of which were subject to changes in activity, and some in size and position.

Again with multiple anodes and cathodes, two identical anodes, *A* and *B*, might be giving out approximately equal currents, but if *A* were much closer to a cathode than *B*, the potential relatively close to *A* could be much less than that at a similar distance from *B*, owing to the difference in potential gradients. In some cases it was possible for a strong anode (or cathode) to mask the effect of a weak cathode (or anode) close to it. Thus the magnitudes of the potential differences could not be taken as a hard and fast measurement of the relative activity of a given anode or cathode. Their relative positions had also to be taken into consideration.

The electrodes were not point electrodes, but had a cylindrical area approximately 1 in. in diameter and 2 in. long. During the surveys, the electrode string was hauled taut, but, because of the conformation of the ship, the distance of an electrode from the ship was not constant. The closest distance the axis of an electrode could come to the hull was $1\frac{1}{8}$ in. The furthest distance was of the order of 3 ft.—this occurred at the stern of the ship when the string was held taut against the bottom of the '*A*' brackets, of the shafts or of the rudder. Also, it was not possible to hold the electrodes against the hull at the bow, and near and between the bilge keels. Thus this type of survey cannot be expected to detect the potential differences set up by the very local

currents that may exist on, say, a rusting steel patch, or at pit holes. In general the size and separation between anode and cathode must be appreciable for detection.

The maximum experimental error in zero corrections was of the order ± 3 mv., the chief cause being the change of electrode potential with temperature. The temperature gradient in the sea water in Bedford Basin, as given by bathythermograph surveys was often 10° to 15° F. for the first 25 ft. of water, during the summer months. In early spring and winter, this gradient was much less and the zero error smaller. Small errors in zero were caused by the variation in distance of the reference electrode from the ship. This distance was usually between 150 and 250 ft., dependent on wind and tide. The error introduced by the use of a millivoltmeter instead of a potentiometer to measure the potentials was less than 1%, the resistance external to the meter being approximately 15 ohms. Chloride ion concentration will affect the electrode potential of the silver – silver chloride, but any differences in concentration at the site of the experiments were not considered very significant.

The error in the relative values of the potential between consecutive readings was much less than ± 3 mv. In fact the agreement between values taken several hours apart was good, provided a large temperature gradient was not present or the ship was not in a state of rapid change such as occurred soon after being undocked.

## Cathodic Regions

Although anodic regions on a hull are often "too well" defined by severe pitting and rust deposits, direct information regarding the cathodic regions stimulating this corrosion cannot be obtained from visual inspection in drydock. Yet such information is essential to a comprehensive picture of the phenomena of corrosion, and consideration of the relative importance of the causes of the cathodic regions may point to possible remedies.

Since information concerning these regions can be obtained by potential surveys and frequent reference will be made to them, it has been considered advisable to anticipate results somewhat by discussing briefly the following causes which may give rise to cathodic regions:

(*a*) The negative pole of a galvanic couple between dissimilar metals.

(*b*) The effect of the e.m.f. between bare and painted steel, the latter with rare exceptions being the more cathodic.

(*c*) The effect of intermittent wetting of bare steel by sea water, such steel being cathodic to bare steel that has been permanently immersed.

(*d*) The effect of differences in oxygen concentration. This, in general, is such that the steel area at which the oxygen concentration is greatest tends to be cathodic.

(*e*) The effect of the e.m.f. between bare steel and steel coated with millscale, the latter being the more cathodic.

In general, the major galvanic couples on a ship are zinc to bronze, zinc to steel, or steel to bronze, zinc being the most anodic material and bronze the most cathodic. The greatest concentration of bronze occurred at the propellers, and during a survey potential measurements were taken close to them. Many outlet fittings, e.g., valves, were also made of bronze, but were recessed in the hull. The search electrodes did not enter their negative field, so the effects could not be followed. The electrodes could usually enter the negative regions of the zinc-to-steel couple. The potential measurements at the bare areas provided a useful criterion to determine whether or not the ship was rusting. If all bare steel areas were found cathodic it was assumed that the ship was cathodically protected, at the expense of the zincs.

The effect of (*b*) has been found in a number of these surveys, sometimes to a marked degree. In preliminary surveys on another vessel it was found that the potential reading at a patch anodic when bare changed to cathodic after painting with one coat Anti-Corrosive and one coat Anti-Fouling compositions. The existence of an e.m.f. between bare and painted steel has also been shown on models by the presence of a current flow between bare and painted steel, even when the pieces of steel used were cut from the same sample.

The effect (*c*) is probably a particular case of effect (*d*). In model work it was observed that when a dry piece of steel, clean or rusty, was continuously immersed in sea water its potential changed over 200 mv. with time, becoming more anodic. If the wet steel were again exposed to the air for a short time, the potential on reimmersion was less anodic than just prior to exposure, even though the steel had not been allowed to dry. In the ship the effect (*c*) was observed by holding a wet search electrode casing against a bare patch on the hull just above the water line. Large negative readings were obtained, in some instances greater than 175 mv. (the limit of the measuring instrument) with respect to the distant reference electrode. The search electrode held against the hull just below the water line gave much smaller readings, usually negative. With a wet electrode held just out of the water, and not touching the hull, very small readings were obtained as might be expected owing to an increased resistance path.

The effect (*c*) can occur only near the water line, and in general the effect (*d*) would be greatest here owing to the presence of the air–water interface. Thus, in the absence of other stronger cathodes, it is to be expected that a narrow strip along the water line will be cathodic, and hence protected to some degree against rusting. However, a slight change in draft will alter the position of the protected area and the area formerly protected will begin to rust, with the result that this water line region is usually rusty. The cathodic intensity at the water line will be affected by the hull condition and by the amount of intermittent aeration and wetting due to waves (for the latter reason the approximate amplitude of the waves, crest to trough, has been noted for each survey).

Only a small amount of millscale was present on this ship, and none after sandblasting. It is well known that millscale will stimulate the corrosion of exposed steel areas. In model experiments cathodic regions have been shown to be present at areas of steel coated with millscale.

## Brief History of H.M.C.S. Quinte Prior to Trials

The trial ship was a Bangor-class minesweeper, H.M.C.S. *Quinte*, built at North Vancouver, B.C. and commissioned on August 30, 1941. Its over-all length was 180 ft., beam 28 ft. and gross tonnage 664. The ship was of steel construction and had two bronze propellers. It arrived at Halifax, N.S. (via the Panama Canal) on November 14, 1941, and was then employed on convoy duty in the North Atlantic. In December 1942 it grounded and sank. Salvage operations were carried out from January to April 1943. While the ship was in drydock from December 12, 1943, to April 17, 1944, the damaged plates were repaired or renewed; the hull hand-cleaned with wire brushes, painted with a coat of Anti-Corrosive (A/C) (iron oxide pigment) and a coat of Anti-Fouling (A/F) compositions, and new zincs fitted. The last drydocking, prior to the present trials, was made July 4-6, 1944, for inspection purposes. The hull also was touched up with A/C and A/F paints. The ship then operated in the Bay of Fundy until the end of July 1945, when it sailed to Halifax and remained at a jetty from August until the trials began in March 1946.

## Drydocking Program

This program consisted of a series of five drydockings, during which the hull was treated to provide the desired over-all experimental factors. The sequence of these drydockings was such that the following could be determined: the effects of air exposure alone on a ship that had been long out of refit; the effects of fitting new zincs on such a ship; the behavior of a well painted ship having clean propellers, first without then with zinc anodes fitted; and finally the effect of coating the propellers. In Table I is a tabulated summary of these treatments, which will be more fully discussed later.

## Survey of Ship in Initial State

This survey, Fig. 2, was carried out prior to the program of drydockings, on a ship that had been out of drydock for about 20 months, the underwater hull having undergone the normal painting treatment and zinc fitting while in drydock. The ship had spent most of the time berthed at jetties and had only partial service at sea.

For this survey, the over-all potential differences were small. No anodic activity at zinc positions was apparent, although it was subsequently found that about 60% of the original amount of zinc fitted to the ship almost two years before was still present. This inactivity of the zincs was caused by the seepage of sea water breaching the metallic contacts at the interfaces between the zincs, hull, and retaining bolts, and by the formation of a heavy adherent

TABLE I

| Drydocking | Period | Weather | Treatment | Subsequent time in sea |
|---|---|---|---|---|
| First | 48 hr. | Fair, temp. 25° to 50° F. | Air dried | 15 days |
| Second | 48 hr. | Generally fair, 30° to 50° F. | Air dried, 20 new zinc anodes fitted. | 21 days |
| Third | 19 days | Dry majority of days. Cool and clear. Four days steady rain | Hull dry sandblasted, including propellers. Painted 1 coat A/C (Bituminous base); 2 coats A/C (iron oxide pigment); 1 coat A/F.* All zincs removed | 11 days |
| Fourth | 7 hr. | 48° to 55°. Overcast | 22 new zincs fitted | 5 months |
| Fifth | 24 hr. | Overcast and cool | Propellers painted, zincs cleaned | |

* *A/C—Anti-Corrosive.*
*A/F—Anti-Fouling.*

corrosion film on the zinc surfaces. The observed anodic regions, therefore, must have been due to the solution (i.e., corrosion) of the steel at the exposed areas. Subsequent visual examination of the hull showed that the hull was bare of paint at the regions found to be most anodic. Small localized anodic 'hot-spots' (e.g., the many small pits and corroded rivets) were not picked up individually. This is understandable since the potential difference recorded was the average over the area of a search electrode, which was large when compared with the size of some of the anodic sources, and also because at most positions the distances separating the electrode from this type of anode would be relatively large compared with the anode size.

The small negative readings near the propellers indicated that the current to it was minor and, being much less than in a later case when the ship had been freshly painted and propellers cleaned by light sandblasting, demonstrated the protection given by the 'chalking film' coating the propellers. This coating was observed when the ship was drydocked. The general state of the hull is shown by Figs. 23 and 24. It may be seen that extensive damage has been done by corrosion.

## Initial Drydocking, March 20-22, 1946

An inspection of the hull showed that the positions of the larger corroded areas, occurring chiefly where the paint film had been damaged by chafing, agreed well with the anodic regions found in the close-up survey of March 15. Other smaller areas, coated with heavy layers of rust, were found where the ship had been supported by bilge and keel blocks, and apparently left unpainted, at the previous drydocking. The excessive pitting caused by the omission of painting such areas can be seen in Fig. 25. Many rivet heads

were badly rusted and several were leaky. Elsewhere, although the plates had been badly pitted prior to the last painting, the amount of new local pitting on the plates was not excessive, considering the time since the ship was last drydocked. The port 'A' bracket and both propeller shafts were coated with heavy deposits of rust. The starboard 'A' bracket had been renewed during the last refit and was in a better condition. It was covered by an almost intact coating of millscale.

Fouling was not excessive and consisted of weeds and mussels. The weeds were spread over the hull as small tufts which were 1 to 3 in. long. The concentration of the tufts was largest near the keel amidships. The mussels were mostly scattered, but had formed clusters around some of the larger outlets. Both propellers were chalked with a fairly thick adhesive grey-white coating. Although a large percentage of the original mass of zinc was still present, all the zinc anodes looked very inactive and were coated with corrosion products.

## Surveys of Ship After Initial Drydocking

The survey, Fig. 3, was begun within three hours of undocking. Comparing Fig. 3 with Fig. 2, it is evident that a very marked change in distribution and intensity of anodic and cathodic regions had taken place. The potentials of the water line section had changed from negative to positive. The propeller shafts and part of the keel had become more anodic. At the stern and near the bow, strong negative readings were obtained. The strong anodic readings occurred where the steel was bare of paint (as shown by heavily coated rust patches on the ship in drydock), whereas the intense cathodic areas occurred where the paint was almost intact, and near the propellers.

The reversal of potential at the water line and the increased strength of anodic and cathodic readings is considered an excellent illustration of the important part played by cathodic polarization in retarding corrosion rates. For Fig. 2 the polarization would have reached a more or less steady state, the ship having been continuously in the water for about two years. Immediately after undocking, the ship would be in a depolarized condition. Because the cathodic area (especially the painted area) was large in comparison with the anodic area (bare steel), cathodic polarization would not immediately reach the state it had prior to air exposure. The measurable differences in potential between anodic (bare) and cathodic (painted) areas were thus much larger than prior to air exposure.

In the absence of polarization, the large painted areas would (after two years water soaking) have relatively low over-all resistance and would therefore be capable of receiving a large current. The effect of other cathodes could be masked by this bare-to-painted-steel current, accounting for the absence of the water line cathodic region. The current flow to the water line cathode might be the same in both cases, but after drydocking it would be a much smaller fraction of the total current. It is also to be expected that polarization of the painted areas would again occur with time. Some evidence

of this may be seen in the decrease of negative values at the overlap readings near the stern, in a time interval of about two hours. A survey showed it had definitely occurred by the end of seven days.

Fig. 4 shows the survey results 15 days after undocking. From this survey it is apparent that the hull tended to return to its rather 'passive' state prior to air exposure, and corrosion to proceed at approximately the steady rate presumably existing prior to air exposure.

The fact that air exposure does depolarize the cathodic regions, stimulating anodic activity on reimmersion of the hull, is of importance for merchant ships which suffer major changes in draft, exposing to the air, and subsequently immersing, large steel surfaces (both painted and bare).

## Second Drydocking, April 7-9, 1946

The condition of the hull appeared to be approximately the same as in the last drydocking. Some of the looser rust had fallen away and some of the weeds broken off. Old zincs were removed and weighed. Several precautions were taken when fitting the new zincs. The hull was cleaned to shiny steel at all zinc positions by the use of air-driven brushes and chipping hammers. Zincs were fitted around outlet positions, rather than inset in the openings where reliable metallic contacts are difficult to obtain. Washers were welded to the retaining nuts and wherever possible studs were screwed and then welded to the hull. Although no attempt at a special watertight fitting was made, some ozite (a bituminous substance) was applied to a small area surrounding one of the nuts on each of eight zincs to test it as a watertight seal on the outer surface. The new zincs were weighed before the final fitting.

## Surveys of Ship after Second Drydocking

The close-up survey, Fig. 5, was begun within three and a half hours of undocking the ship. The most distinctive feature of this survey was the presence of pronounced anodic peaks at the positions of the new zincs. Otherwise, comparing this survey with that obtained immediately after the ship was subjected to air exposure alone (Fig. 3), it can be seen that the hull had a marked tendency to assume the same distribution of anodic and cathodic areas. Thus there were anodic regions at the water line on both sides amidships, and the previously intense cathodic regions were again strongly cathodic (with the exception of the effects at the extreme stern caused by the presence of the new zincs). The slightly anodic regions near the keel at the earlier date had become slightly cathodic.

Three days after undocking, a change from large positive to large negative potentials had occurred in the midships region near the water line, and strong positive readings were found only in the immediate vicinity of zincs. In addition, the less cathodic regions of Fig. 5 had become more cathodic, while the intense cathodic regions had become less cathodic, especially in the region between the groups of zincs just aft of midships and at the stern, where

small positive readings were obtained. This condition remained approximately constant for the next 14 days. Fig. 6 shows the result of the survey at the end of this time.

This behavior of anodic and cathodic regions is explicable on the hypothesis that the various parts of the ship had a different susceptibility to the formation of resistant films by an electric current. The exact nature of the film does not affect the following argument. Since, as seen in Fig. 5, intense anodic peaks occurred in the vicinity of all the zinc plates, it may be taken for granted that the zinc plates were the chief anodic source of current. Current from these plates would initially flow to areas having the greatest tendency to be cathodic, i.e., areas that were cathodic under similar main hull treatment of exposure to air. Immediately after undocking, these cathodic areas, having been depolarized by exposure, had low enough resistance to absorb the current given by the zincs, and in addition to take some current from the bare steel itself. The bare steel areas would not, however, emit as much current as formerly (e.g., Fig. 3) on account of the opposing potential of the zincs with respect to these steel anodic areas. With the current flow a resistant film built up over the original cathodic areas, thus decreasing the current to them. This in turn allowed the zincs to counteract more effectively the current from the anodic steel areas and, in time, to reverse the current flow so that areas formerly anodic became strongly cathodic, e.g., amidships (Figs. 5 and 6). They became, in fact, more cathodic than the painted areas. This was probably due to the absence of the potential drop which was present at the paint barriers. The maximum time required for this transformation was less than three days—the same order of time in which polarization changes occurred after the initial air exposure.

It is of interest that the anodic region between the zincs at the stern and those nearer amidships began to develop within three days of undocking. An experiment was carried out on the seventeenth day to determine whether this anodic region was due to (*a*) the corrosion of steel in this vicinity, or (*b*) formation of a resistant film by the zinc-to-hull current, which, altering the potential distribution, shifted the zero potential surface so close to the cathode that the search electrodes were unable to enter its negative region. A current was passed from the hull to an external cathode, and a survey made immediately after the current was broken. The cathode used was a copper plate (16 ft. by 1½ ft. by 1/64 in.), one side insulated with ozite. It was rigged closely under the hull, ozite side out. The hull was connected to the positive terminal of a 4 v. storage battery. The passage of a 30 amp. current for 1½ hr. resulted (Fig. 7) in a reversal of polarity of the region in question (near the stern tubes), giving a potential distribution somewhat similar to that obtained there immediately after undocking (Fig. 5). This reversal of polarity indicates that process (*b*), the development of the resistant film, was the chief cause of the change in the potential in this region. It is to be noted that the effects on the hull of the passage of current diminished rapidly.

This is seen in the difference in values at the overlap of potential readings (Fig. 7) near the stern, taken approximately an hour apart.

During the survey (Fig. 5) potential readings were also taken with the electrode string slacked off in the region near the propellers so that the distance from the propeller blade to the nearest electrode was approximately a foot, and the distance from a zinc to the closest electrode was at least six feet. The readings obtained with the string held in this position were all strongly positive, indicating that the current to the chalked propellers was relatively small.

## Third Drydocking, April 30 to May 18, 1946

The hull seemed in essentially the same condition as at the time of the last inspection. The new zincs showed signs of active attack and corrosion products had adhered to their surfaces. They were removed, cleaned of corrosion products, and weighed. The hull was sand blasted from the keel to the 8 ft. 6 in. draft mark at the bow, to the 9 ft. 6 in. mark at the stern, and to the bottom of the top rubbing streak amidships. The propellers were also cleaned by sandblasting. To avoid rusting due to atmospheric conditions, no sandblasted area was left unpainted overnight. During wet weather the ship was left untouched except for minor places such as the eddy plates, keel, and bilge block positions, which were protected from the rain and could be painted immediately after cleaning. The hull was painted with one coat of bituminous paint, two coats of iron oxide pigmented A/C paint, and one coat of A/F paint. The bottoms of the numerous pits present in the steel were difficult to fill with bituminous paint, the thickness of which also handicapped an even application. This difficulty was overcome by applying the paint with an improvised spray gun working on the aspirator principle, held two feet from the hull, instead of by brush. After the application of the A/C paints, the ship was undocked and moved forward on its keel blocks to permit cleaning and painting of the areas on which the ship had rested. One and a half hours was required to apply the A/F paint, and the ship was undocked two hours after the painting was finished.

## Survey of Ship after Third Drydocking

Within four hours of undocking, the hull was, in general, only slightly anodic, Fig. 8, but anodic peaks occurred at some outlets, at the asdic dome and at the broken bilge keel on the starboard side, i.e., at all the places where the paint film was applied to poorly prepared surfaces. (The nature of these places did not permit cleaning by sandblasting or by air driven wire brushes.) A fairly strong cathodic region occured at the stern. The positions of the peaks indicated that the current flow was essentially from the vicinity of the outlets, etc., to the propellers, and the strength and polarity of the peaks indicated that it was due to exposed steel rather than to the nonferrous fittings.

Three days after undocking, the hull showed increased anodic activity, especially on the port side near the water line. This increase in activity was undoubtedly due to the abrasion of the paint film in this region (the ship having been berthed at its jetty, port side to). Anodic regions at the asdic dome and at the main injection valve were the only indications at outlet positions. The two small anodic peaks present, about 60 ft. from the bow, were probably due to damaged paint at a bilge or keel block. With the increase in anodic intensity, there was a corresponding increase in cathodic intensity at the stern, further evidence that the current was mainly caused by the hull-to-propeller galvanic couple. Nine days after refit, the survey (Fig. 9) showed the state of the ship to be essentially the same, with the addition of an anodic region at the water line on the starboard side. The increase in activity was, undoubtedly, again caused by the abrasion of the paint, the ship having been berthed starboard side to at its jetty.

To show that the anodic regions were points of low resistance, a current (about 30 amp.) was passed to the hull from a copper strip ($1\frac{1}{2}$ by 16 by 1/64 in.) placed athwartships at the stern. The ends of the copper strip were held 10 ft. below the water level. The hull was then surveyed, Fig. 10, with the current flowing. Strong cathodic peaks occurred at the positions of the previous anodic areas, Fig. 9, showing that such areas were of low resistance. Cathodic peaks also occurred at some of the outlet positions, e.g., main injection. The positive region at the stern was due to the copper strip anode. An important result of this test was evidence that the hull, in a relatively good paint condition, could readily be 'cathodically protected' by means of a current flow of about 30 amp. When the current was broken, the prior disposition of anodic and cathodic regions returned, with some changes in intensity.

The results of the above surveys indicated that the main current was a hull-to-propeller current, and that this current was probably greater in magnitude than it had been when the hull was in a poor paint condition and the propellers chalked. Evidently in the latter case, the coating on the propellers was sufficient to reduce the hull-to-propeller current to a fairly low value even though a much larger bare steel area was available.

## Fourth Drydocking, May 29, 1946

Paint was badly stripped on port and starboard sides near the rubbing streaks, owing to damage sustained while the ship was secured to its jetty. Where the paint was missing, rust was present. Rust had also occurred at positions where the ship had sat on the bilge and keel blocks during the last part of the previous drydocking (i.e., after the ship had been moved forward on blocks). These places were shown by the marks of the wood grain in the paint. The rusting had occurred mostly in streaks where the bituminous paint had cracked under pressure. (In general, the potential surveys did not show these places of rusting as strong anodic regions. The only indication of anodic activity was the occurrence along the keel line of slightly greater

than average anodic potentials, showing that if an intense anodic region, not due to a zinc, was detected, the steel must have been entering solution at quite a fast rate from a fairly large area.) The paint apparently had poor adhesive qualities and was brittle. A tap with the end of a wrench caused flakes of paint up to half-inch square in size to come off, revealing a dry, shiny steel hull.

Where paint was undamaged by chafing, etc., it had prevented further action at rivets and old pits. Active pits could readily be detected, but occurred only at a few scattered places.

The condition of the A/F paint was not good. Even though the ship had been put in the water with the A/F paint in a tacky condition, the paint was dry and hard when the ship was hauled out of the water. There were also a number of small circular patches where the paint was missing, especially between the bilge keels. This was caused by the formation of salt droplets on the A/C paint during the previous docking, after the position of the ship in its cradle had been changed. When the ship was hauled out (in the rain) most of the salt water ran off the hull, or was washed off by the rain. However, on the protected areas, e.g., between bilge keels, the sea water ran into droplets and was not washed off. These droplets were dry when the A/F paint was applied, but the crystallized salt deposited by the drops prevented the A/F paint adhering to them. The hull was free from all animal and vegetable life.

All the damaged paint areas were touched up with one coat of A/C and one coat A/F, with the exception of some of the water line areas on the port side amidships and forward.

In fitting new zincs a different method was tried in an attempt to make and maintain a waterproof metallic contact between the hull and the zinc. Securing bolts were used to make the contact. Rubber washers between the zinc and hull, and an ozite coating over contacting nut or bolt heads were used for waterproofing. Steel washers were welded to all retaining nuts, or studs, and the threads were tinned with solder. All zincs were weighed to the nearest ounce and their approximate exposed area determined.

## Surveys of Ship after Fourth Drydocking

A survey was made within a day of undocking (Fig. 11). Anodic peaks were present only in the vicinity of the zincs. The main cathodic region occurred at the stern while lesser cathodic regions were found at the asdic dome (not fitted with zincs) and near the water line on the port side. (This side of the ship had been next to the jetty overnight, and the touch-up painting was not completely applied on this area.) The distribution of anodic and cathodic regions indicated a main current flow from zinc to propeller, a minor current from zinc to hull, and no current from hull to propellers.

Not all zincs had noticeable positive peaks. Some peaks were absent at the stern, and those present were small compared with the peaks obtained after the second drydocking (Fig. 5), when the propellers were chalked, and

the zincs put on a hull in poor paint condition. The absence of positive peaks was not considered to be due to a small current flow from the zincs in this region, but rather to the position of the zero equipotential surfaces with respect to these zincs. The main current flow was from the zincs to the propellers. The zincs were in scattered positions over the hull, and the zero equipotential surfaces of the composite battery ran closest to those zincs nearest the cathodes, i.e., those near the propellers, even though the current density at these zincs may have been slightly higher than at those further away. In the case of the second drydocking, however, the main current was from zincs to hull rather than from zincs to propellers, which caused the zero potential surfaces to lie close to the propellers and away from the zincs in this region. This was indicated by the presence of intense cathodic regions on the hull itself, and by their absence near the propellers when search electrodes were held within a foot of them.

Surveys made 4, 9, 12, 19, 28, and 34 days (Fig. 12) after undocking showed the following characteristics: positive peaks only near zincs; an increased spread with time of the positive region at the stern and a corresponding decrease in the negative region near the propellers; a general increase in intensity of the negative potentials on the hull; and a decrease in the negative peak at the asdic dome with time. The increased negative potentials on the hull occurred particularly at the water line, where the paint film was abraded first on the port side and then on the starboard side—the ship was berthed for only a short time starboard side to. On and after the ninth day, the negative pole of the zinc–propeller current was to be found only by lowering the electrode string away from the hull towards the propellers. (The negative readings obtained near the propellers do not appear in the plotted results, which were for the electrodes held as close to the hull as possible.) The spread of the anodic region at the stern was of special interest in that it showed the change that can occur in the position of the zero equipotential surface. As stated in the preceding paragraph, this surface at first ran close to the zincs near the stern. It then moved further away from the stern zincs and nearer to the propellers with increase in 'effective' length of path due to current flow between stern zincs and hull. Thus it could not be said, when discussing Fig. 11, that the stern zincs were producing a relatively small current, nor, from the results shown in Fig. 12, that the propellers were not receiving current. This demonstrates the necessity of exercising care when interpreting the results of this type of survey. On the thirty-fourth day an inspection of the water line showed the visible bare patches of the hull to be bright and free from rust.

Thirty-six days after undocking, Fig. 13, a change in anodic peaks had occurred. Additional anodic peaks had appeared near the water line on the port side in previously cathodic places, while the intensity of the cathodic peaks on the starboard side had increased. Two factors tended to bring this about. (*a*) The propellers had been recleaned the day before the survey by a diver using an air-driven brush. (*b*) The ship had been berthed starboard

side to. The net effect was to give the zincs more work by exposure of a larger area of steel and by removal of some of the deposit formed on the propellers during the five weeks since undocking. The presence of an anodic region on an area of steel surface where no zincs were present showed that the zincs under the new load were unable to protect the hull 100% effectively. As there were only two days between this survey and the previous survey, it is probable that the cleaning of the propellers had had the greater effect. The increase in area of exposed steel would only be slight, as the ship had already been subjected to abrasion on that side for a few days. The additional current required to prevent the rusting of the steel could not be supplied by the zincs because of the continued formation of the corrosion product on their surfaces. This product forms a resistant layer which decreases the available current as time goes on.

Considering the results obtained with the new zincs on a poorly painted ship, it was surprising that (non-zinc) anodic regions should appear so soon, when only a relatively small amount of bare steel was exposed to the sea, and especially as the zincs seemed equally active for both cases. This is a further demonstration of the desirability of counteracting the influence of the propellers, since in the case of the poor paint job the chief factor favoring protection was the chalked condition of the propeller.

Why the anodic region caused by the solution of steel should first appear on the port side, while the starboard side remained cathodic, is also a minor question. Possibly the zincs could supply only sufficient current to the propellers and painted areas to maintain their potential equal to that of unpolarized steel. Then local action could occur on the steel, and the cathodic regions on it would be those having greater available supply of oxygen and the greater intermittent water line exposure. The paint on both sides was damaged near the water line, but the damage on the port side was at a slightly greater draft than on the starboard side, as the ship had had a shallower draft when berthed port side to. Another explanation could be the difference in length of the effective current paths in the sea from the zincs to the exposed areas on the two sides.

Surveys made 44, 55 and 65 (Fig. 14) days after undocking showed further increases in anodic regions on both sides of the ship where steel was exposed. Visual inspection showed the bare areas at the water line to be rusting and there was some evidence that the length of the equivalent current path might play a part in determining which bare spot would rust first. The cathodic regions near the propellers showed a small decrease in area and intensity. The development of anodic sources on the steel itself and a decrease in the zinc efficiency changed the relative geometrical positions of sources and sinks, and caused a shift in zero potential away from the propellers. This shift would tend to accentuate the apparent weakening of the zincs at the stern, i.e., some of the zincs might still have been quite active, although their anodic peaks were masked by the nearness of cathodic sinks—the propellers. (From an inspection of the zincs at a later drydocking, it was evident that five of

the zincs at the stern had not remained active very long owing to a failure of hull-to-zinc contact.)

In order to obtain more information on the masking effect, an attempt was made to chalk the propellers by passing a current of about 30 amp. for about 50 hr. from a copper plate placed just below the propellers. The survey results are shown in Fig. 15 (68 days after refit). A marked change from the previous survey (three days earlier) was observed in potential distribution.

The change would have been more striking but for a lapse of time between the stoppage of the current and the survey (approximately 14 hr.). The anodic zones at the stern had reappeared and were still fairly strong about 17 hr. after the passage of current. In an additional two hours, the region in the vicinity of the propellers had begun again to show negative values, hence the effect was not all permanent. Part of the effect was probably due to permanent chalking, the rest to temporary deposition and polarization. Also, some of the zincs may have been reactivated by having their corrosion product loosened, which would allow them to furnish a greater current. During the survey the bare patches at the water line became more positive with time, as shown by the two sets of readings taken on the starboard side just over three hours apart. These readings indicate that, had the survey been conducted sooner, the whole water line would have been fairly strongly negative and the hull cathodically protected. It is thus again apparent that an additional current of approximately 30 amp. gave complete cathodic protection to the hull.

Seventy-five days after undocking, Fig. 16, the ship had reverted to its approximate state prior to the passage of current. If anything, its condition had deteriorated, as shown by a decrease in the anodic peaks at most of the zincs, and a spread of anodic zones near the water line. The zinc anodic peaks at the extreme stern did not decrease in intensity, indicating that the propellers were somewhat chalked by the passage of the current. The cathodic intensity very near the propellers was less than that prior to chalking, but greater than that immediately afterwards.

Seventy-six and seventy-seven days after undocking, 19 of the zincs were cleaned by a diver using a small wire hand-brush; 15 on the first day and 4 on the second day. This cleaning was done to determine which was the more important factor in decreasing the activity of the zincs: (*a*) the corrosion film formed on the surface of the zincs; or (*b*) a poor electrical contact between the hull and the zincs. If (*b*) were the major cause, cleaning the surfaces of the zincs would have little effect, whereas if (*a*) were the cause, a rejuvenation of the zincs would be expected. (The diver's reports on the comparative depth of pitting on the zinc plates were not very consistent, the general report indicating that the zincs were not very badly pitted, and that the corrosion film on the zincs was thin (about 1/16 in.) and fairly easily removed.)

A survey, Fig. 17, carried out on the second day, showed a definite increase in anodic peaks near the zincs. This indicated that (*a*) was the more important factor in the decrease in zinc activity. No negative readings were obtained

when the electrodes were lowered into the immediate vicinity of the propellers, although the potential readings were only slightly anodic in this region and the gradient such as to indicate a cathodic sink in this area. A change from anodic to cathodic values occurred in many places over the hull, a noticeable exception being the starboard side water line. Why the starboard should remain rather extensively anodic while the port side became mostly cathodic is unknown, but the occurrence is suggestive of Fig. 12, where the port side became anodic while the starboard side remained cathodic. The explanation may again be that the zincs were just sufficiently active to polarize the propellers and painted areas to the potential of steel, allowing local action on the steel to take place. In this case, after the diver started to clean the zincs, the port side was next to the jetty for about 20 hr., as compared with 2 hours for the starboard side. The most important fact is that with only one major change in the general state, i.e., the removal of the corrosion film on the zincs, the ship, which prior to the change was poorly protected, became almost fully cathodically protected.

Eighty-four days after undocking, a week after the cleaning of the zincs, the anodic regions (Fig. 18) of the steel near the water line had increased in area and intensity, while those caused by the zincs had decreased. The decrease again indicates the undesirable formation of the resistant layer on the zincs and the rapidity with which it will reduce their effectiveness.

Surveys made 99 and 112 days after undocking showed: the development of an anodic region near the bow, the first definite evidence of the failure of the paint film, other than where damaged near the water line; a progressive decrease in zinc anodic activity; a change in depth of anodic peak positions, due to an increase in draft of the ship; and a general decrease in intensity and area of most cathodic regions, except for the beginning of cathodic regions at the water line on the starboard side. The last effect was probably partly caused by the increase in draft, but it indicated that the propellers had become chalked again, and were not stimulating the corrosion of the steel to the same extent as previously. This point was tested by recleaning the propellers on the 113th day and surveying the following day. (The cleaning was done by a diver using a rotary air-driven brush. During the subsequent drydocking the outline of where the diver had cleaned could be seen, and it was estimated that while about 30% of the port propeller had been fairly well cleaned, not more than 5% of the starboard one had been cleaned.) The results of the survey showed an increase in anodic activity and the disappearance of cathodic regions at the water line, i.e., cathodic control of the current to the propellers.

On this day another test was made. Readings were taken both with the propellers stopped and with them rotating at approximately 5, 40, and 60 r.p.m. The electrode string was held slack over the stern so that No. 1 and No. 8 electrodes were 24½ ft. deep in the water. The readings were, in general, about 4 mv. more negative with the propellers turning than when stationary (the average reading with them stopped being about 1 mv.). There was, however, very little difference in readings obtained at the different

speeds. Apparently a very slow rotation was sufficient to make the difference, and increasing the speed had little effect. Once the engines were stopped, the readings returned to their normal value in about five minutes and the process could be repeated by further turning and stopping. Almost immediately after the propellers started turning, the readings increased negatively. Two possible causes were: (*a*) depolarization effects of moving water on the propellers and the steel, and (*b*) improvement of contact between propeller shaft and hull by turning Either of these causes could increase the current between the hull and propellers, and search electrodes placed in the area near and below the propellers would measure the relative increase in negative potential at the negative pole, i.e., at the propellers. Four days later, in an attempt to differentiate between (*a*) and (*b*), two phosphor-bronze bars, about 2 in. wide, $\frac{1}{8}$ in. thick and 15 in. long, were used to connect the hull electrically to the section of each shaft carrying the propellers. The contact areas were well cleaned. Potential measurements near the stern were made with the electrodes No. 1 and No. 8 held $24\frac{1}{2}$ ft. deep. No differences in reading were observed whether or not the shorting bars were connected. Thus (*a*) was the probable explanation. The effect of the turning propellers had decreased from that of the previous survey, the difference being only about $2\frac{1}{2}$ mv. with the electrodes in similar positions. These measurements were carried out five days after cleaning the propellers and indicated that the propellers had become more chalked in this time. On the same day a complete survey of the ship was made with the propellers stationary, followed by a partial survey with the propellers turning at about 40 r.p.m. and a repeat over the same section with the propellers stationary. The agreement between the two sets of readings, taken approximately two hours apart with the propellers stationary, was in general good. The anodic readings obtained with the propellers rotating were usually more positive (order of 6 mv.) than either set, while the cathodic readings generally tended to become more positive (2 mv.) towards the bow and more negative (3 mv.) towards the stern. Two complete surveys were made six days later, one with the propellers turning, the other with them stationary. Agreement with the previous results was obtained, except that the magnitude of the changes was less. These results suggest that for a ship with relatively clean bronze propellers, the corrosive effect on the steel is accelerated when the ship is under way, and only a few revolutions of the propellers per minute are required to produce this acceleration. They also provide another indication that the state of the propellers controls, in general, the current going to the propellers.

In addition, the above surveys showed increased anodic activity of the steel, both at the water line and at the bow, and decreased zinc activity. The presence of a peak near a zinc indicated that the contact between it and the hull was still good. To determine more readily the number of zincs having a good metallic contact, the zincs were recleaned (by a diver using a small wire handbrush) 125 days after undocking, and the ship was surveyed the following day. Increased anodic activity was noted for zincs situated at

positions forward of the shaft entrances, indicating that their contacts were good. The zinc anodic regions at the stern also increased, but because of the structure of the ship, the short distance between zincs, and the presence of the propellers, it was not possible to distinguish the anodic region of each zinc, hence the number of these still making contact was not determined. A marked decrease in anodic activity of the steel also occurred, both at the bow and at the water line, giving another demonstration that cleaning the corrosion film off the zincs increased the cathodic protecting power of the zincs. The zincs were given only a cursory cleaning by the divers. On drydocking a month later it was seen that pits in the plates, in some instances over a quarter of an inch deep, had not been cleaned out. This superficial cleaning explained the rather rapid increase in the steel anodic regions and the decrease in the zinc anodic regions found during the survey made eight days later.

The last survey of this group was made 152 days after undocking, and three days after the ship had been decommissioned. The survey was, thus, for a dead ship having no stray currents from its electrical supplies, no heat, and no discharge of hot water. The result of this survey is shown in Fig. 19. No major changes in the potentials surrounding the ship were found; the only noticeable changes were due to a further decrease in activity of the zincs. This illustrates that the potentials surrounding a ship are chiefly affected by the condition of the external hull and fittings (e.g., the condition of the paint, zincs, and propellers) rather than by the internal condition of the ship.

## Fifth Drydocking, October 29-30, 1946

The visual inspection showed the following: (*a*) That the prime paint coating was completely perished and, when dry, required only a light push with a fingernail to crumble it, revealing bright steel surface below. (*b*) A rusted water line region, 2 to 3 ft. deep. (*c*) Many small rusted areas (usually from ½ to 2 sq. in., with some up to 10 sq. in.) whose shape and disposition indicated that they had occurred where the paint had flaked off the hull. These areas were scattered over the whole hull with a somewhat greater concentration at the bow (Fig. 26). They did not occur on rivets, but seemed to favor flat and previously undamaged regions of the plates, i.e., very few occurred at the location of previous pits. The pits below these rusted areas were as much as 1/50 in. deep, with a distinct wall and a very even bottom. (*d*) The majority of the zincs had been subjected to a fairly severe attack (see Fig. 27). The remainder had been only superficially attacked; the reason for this was the failure of the metal-to-metal contacts. (*e*) The propellers were coated with a light film, some of which was difficult to remove with an air-driven rotary wire brush. The pattern of the previous cleaning by the diver, resulting in a lighter coating, could be readily followed. (*f*) While the ship was in drydock, the paint on drying peeled off in many more small areas, especially on the starboard side, which faced the sun. (*g*) The fouling was relatively light except for a layer of weeds formed on the port side from the water line down to a depth of about 3 ft. This side was away from the jetty and faced south

when the ship was at its berth from the end of June on. Some small shellfish (up to $\frac{1}{4}$ in.) had formed clusters near the bow; otherwise, scattered tufts of weeds were the only fouling present.

During this drydocking, the propellers were cleaned mechanically and two coats of a lacquer paint applied over their surfaces. The zincs were cleaned with a wire hand-brush, and at least one of the bolts, or nuts, on each zinc slab recontacted. A few of the zincs were reweighed, to determine from their weight loss the approximate average current for the previous five month period. The zincs chosen for reweighing were fairly typical examples, rather than the most severely eaten (which would have been difficult to remove and replace without breaking). Some of the zincs for which the contacts had failed were also reweighed, for purposes of comparison.

The condition of the hull was such that it could have been readily cleaned to shiny steel in preparation for the application and testing of a different type of paint, but as the ship had been decommissioned and was to be disposed of, no other expenditure was considered warranted. As part of the disposal program, the asdic dome was removed.

## Surveys of Ship after Fifth Drydocking

Four surveys were made following this drydocking. The first survey was completed within $5\frac{1}{2}$ hr. after undocking. The results, Fig. 20, followed the same general pattern as previously obtained when the ship was in a poor paint condition, the zincs active, and the propellers fouled. Intense anodic regions occurred at zinc positions and at the water line where relatively large areas of the hull were bare of paint. A small anodic region occurred at the asdic dome recess, which now had over 100 sq. ft. of steel fairly well exposed. Other regions were strongly cathodic, although less so than those of Fig. 5. Two causes contributed to the decreased strength.

(*a*) The paint condition was worse, with many newly exposed steel areas which tended to be actively anodic. Although their anodic effects were masked, they would still decrease the measurable intensity of the surrounding active cathodes (not polarized).

(*b*) The surfaces of the zincs were well cleaned, but they were not bright and their exposed areas were less.

When the electrodes were lowered close to the propeller, no sign of a cathodic sink was encountered, i.e., a negligible current was going to the propellers.

A second survey (Fig. 21) carried out two days after undocking, showed a marked change in potential distribution. The anodic intensity at the zincs had decreased and, as was to be expected, this had allowed the anodic intensity at the steel to increase. The largest increase in intensity occurred not at the water line, however, but more or less along the whole starboard side, especially towards the bow. The port side at the bow remained cathodic, and no cathodic tendency was detected at the propellers. Thus, the anodic increase

at the steel was not due to an increased current flow between hull and propellers. The above facts, when taken in conjunction with the visual observations of the greater peeling of paint on the starboard side, further illustrate the importance of the current flow from bare steel areas to painted steel areas. Even though in this case the paint was loosely adherent to the steel, it still caused anodic stimulation, i.e., corrosion of the bare steel. At the time of this survey, the painted areas probably had become polarized to a roughly equilibrium value, a condition which would allow the effects of the smaller anodic areas to show up. The decrease of anodic intensity along the water line indicates that the water line cathodic regions had begun to play a more important part. On the day of the survey a strong wind was blowing, causing fairly high waves to lap along the ship, which would accentuate this effect. It is to be noted that the readings at overlaps were rather erratic. This would be expected for a scattered distribution of relatively small anodes.

Thirteen days after undocking, the changes noted in the second survey were more marked. The anodic intensity at the zincs had decreased. This was especially noticeable at the stern, where only a small anodic zone occurred near the rudder. The water line had also become more cathodic. With the exception of the zinc anodic zones, the port side was cathodic, and the starboard side anodic. A strongly cathodic zone was encountered when the electrodes were lowered near the propellers. This showed that the effectiveness of the coating on the propellers had decreased in a short time (less than 13 days). As the ship had been towed (about 10 miles) only at slow speed since the painting of the propellers, and the paint film would not likely have been damaged by abrasion, it had evidently become waterlogged during this period, allowing relatively free passage of current to the propellers. This early breakdown of the coating may have been due partly to the shortness of the drying period before immersion.

The final survey, Fig. 22, was carried out 43 days after undocking, just after the ship had been winterized. Most of the zincs were found to be relatively inactive, especially those at the stern. Cathodic zones along the water line were quite noticeable, accentuated partly by the strong wave action present on this day, which intermittently wet a fairly large area of bare steel at the water line. The draft of the ship was less than normal, exposing bare steel to wind and water. Cathodic regions were present at the stern (the order of 60 mv. within a foot of the blades) and on the port side near the bow, otherwise the steel anodic regions had spread.

## Variation of Hull Potential

The e.m.f. existing between a ship's hull with its composite sources and sinks, and a standard reference electrode (held at least 30 ft. from the hull) has been briefly called the hull potential. This potential depends on the resistance at each anode and cathode as well as on their individual e.m.f.'s with respect to the reference electrode. The resistance at each anode or cathode depends on the exposed area, film resistance, and polarization. Among

these factors the degree of polarization of the cathode is important in determining the value of the potential of the hull with respect to the reference electrode. For instance, an anode may have an area equivalent to, or smaller than, a cathode, yet, because of the increase in resistance caused by polarization, the resultant e.m.f. of the two in metallic contact is not usually the mean of the two individual e.m.f.'s with respect to the reference electrode, but is generally closer to that of the anode alone. This fact is of interest in that it possibly offers a simple test to determine roughly the degree of polarization of the hull. Some such test will be required if cathodic protection is used as a general prevention against the rusting of ships.

To find the relationship between the potential of the hull and the state of the hull, the potential of *Quinte*, with respect to a silver – silver chloride reference electrode, was measured on the majority of days on which surveys were made. The reference electrode was connected to the positive terminal of the voltmeter for all readings, and the ship's deck to the negative terminal. (The connection to the deck was first tested in several positions, without noticeable change in voltmeter readings; thereafter it was made amidships, starboard side, on a convenient lug.) The voltmeter used had a very low resistance per volt (an Avo-meter instrument) and the potentials can be considered only approximate (smaller than would have been the case had a potentiometer been used). They did, however, indicate the general trend of the change in potential with state of hull, as shown in the following examples.

After the third drydocking, when the hull had been freshly painted, the propellers cleaned, and no zincs attached, the potential reading on the first day of immersion was 420 mv., which increased to 500 mv. by the ninth day. That is, on the first day the resistance between reference electrode and propeller was less than that between reference electrode and steel, and the resultant potential was close to that between reference electrode and clean bronze alone, which is about 400 mv. The small value of the potential indicated that the propeller was not polarized to any extent. As exposure of the steel occurred, its resistance (steel to reference electrode) became less, and the resultant potential of the hull changed towards that of the steel. On the ninth day, a further test was made. The hull was connected to the negative terminal and a copper plate in the sea to the positive terminal of a 4 v. battery. A 30 amp. current was passed for an hour and a half. Prior to the passage of current, the hull potential was 500 mv.; on making the current, it jumped to 1040 mv.; an hour and a half later, before breaking the current, it had increased to 1110 mv.; just after breaking the current it was 750 mv.; and about an hour later it had returned to 500 mv. These values show the effect of polarization caused by passage of current.

On the first day of immersion after new zincs had been added to the newly painted hull (the fourth drydocking), the potential of the hull was 750 mv. Compared with the 420 mv. obtained without the zincs, it is obvious that the degree of polarization of the propeller must have been greater in this case. (The ratio of the exposed zinc to propeller area was of the order of 1 : 6.)

With decrease in the activity of the zincs, and increase in exposure of bare steel, the hull potential gradually changed to 550 mv. and for the next four months stayed between 550 and 600 mv., the value depending on the hull treatment during this period—e.g., zincs or propellers recleaned. As shown in the survey, Fig. 11, the hull was cathodically protected when the instrument indicated that the potential of the hull was 750 mv., while rusting occurred at the lower hull potentials.

## Zinc as an Anode in Cathodic Protection—Weight Loss Evidence

This section is included because the supplementary evidence (weight loss) given in Table II shows that cold rolled* zinc, normally fitted, is relatively ineffective as an anode for cathodic protection. For instance, the loss of weight of zinc over a period of about two years, prior to the second drydocking, was about 93 lb., the initial exposed surface area of the zinc being about 13 sq. ft., whereas, for a three week period, the loss of weight of zinc was about 16 lb., the initial exposed area being about 18 sq. ft. That is, if the zinc had maintained only the same average loss of weight for the two year period, as it did for the three week period, not 93 lb. but about 400 lb. would have been used for an exposed area of 13 sq. ft. Thus it is apparent that most of the corrosion of zinc must occur at the initial stage. In the usual case there are two reasons for this: (*a*) poor contact between zinc and hull due to water seepage corroding the zincs at the contacts, and (*b*) accumulation of corrosion products on the zincs. Direct evidence of (*a*) is given in the third section of Table II where it can be seen that the weight loss for the zincs that had poor contacts, due to failure of the watertight seal, was much less than for those whose seals remained intact—though the initial contact between the hull and the zincs with poor seals were as good as those attained normally. The accumulation of corrosion products was apparent from the fact that the approximate weights of the dross removed from the zincs that had been on for two years was 14 lb., and for three weeks was 3 lb.

## General Discussion

To provide a background for this corrosion research, ships were examined in drydock with regard to the extent and distribution of corrosion damage, and to the normal shipyard treatment. The majority of these ships were Canadian warships, and any reference in the following to anticorrosive treatment is essentially to Canadian practice.

This discussion deals with the results of surveys carried out on a warship when secured to a buoy. If the ship had been underway, the corrosion patterns would have been different, as indicated by the surveys made with the propellers rotating. Also the ship, although in commission until the last six weeks of the program, spent most of the time at a jetty and it is to be expected that under other service conditions the corrosion patterns would again have

* *A stock sheet of zinc contained by analysis 0.24% lead, 0.020% iron, 0.13% cadmium.*

## TABLE II

STATE OF ZINCS AFTER THREE DIFFERENT PERIODS

| Zinc positions | Old zincs in service about 2 yr. | | | | Zincs in service April 9-30, 1946 | | | | Zincs in service May 29-October 30, 1946 | | | | Remarks on zinc condition |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Est. original Exposed area, sq. in. | Weight, oz. | Weight left, oz. | Est. weight loss, oz. | Original Exposed area, sq. in. | Weight, oz. | Weight loss, oz. | Average current density, ma./cm.² | Original Exposed area, sq. in. | Weight, oz. | Weight loss, oz. | Average current density, ma./cm.² | |
| Rudder—Stbd. fwd. edge | 117 | 286 | 210 | 76 | 100 | 179 | 14 | 1 | 90 | 193 | 102 | 1.1 | Well eaten |
| Port fwd. edge | 118 | 290 | 177 | 113 | 100 | 176 | 10 | 0.7 | 91 | 198 | 103 | 1.1 | Well eaten |
| Rudder post—Stbd. | Missing | | | | 49 | 80 | 3 | 0.45 | 41 | 98 | — | — | Well eaten |
| Port | Scraps only | | | | 58 | 91 | 6 | 0.75 | 46 | 102 | — | — | Poorly eaten |
| Over stbd. prop.—Inner | 90 | 221 | 148 | 73 | 90 | 203 | 9 | 0.7 | 74 | 211 | — | — | Poorly eaten |
| Outer | 90 | 219 | 104 | 115 | 91 | 208 | 9 | 0.7 | 84 | 214 | 10 | 0.1 | Poorly eaten |
| Over port prop.—Inner | 89 | 203 | 109 | 94 | 85 | 201 | 13 | 1.1 | 79 | 202 | 22 | 0.3 | Poorly eaten |
| Outer | 85 | 193 | 133 | 60 | 89 | 210 | 11 | 0.9 | 84 | 220 | 15 | 0.2 | Poorly eaten |
| Stbd. 'A' bracket—Top | 81 | 172 | 65 | 107 | 80 | 164 | 13 | 1.2 | 73 | 159 | — | — | Well eaten |
| Bottom | 79 | 168 | 70 | 98 | 76 | 162 | 7 | 0.65 | 72 | 162 | — | — | Well eaten |
| Port 'A' bracket—Top | 162 | 355 | 114 | 241 | 81 | 172 | 6 | 0.5 | 73 | 184 | — | — | Well eaten |
| Bottom | — | — | — | — | 78 | 163 | 13 | 1.2 | 64 | 168 | — | — | Well eaten |
| Fwd. mag. flooding—Port | 77 | 92 | 38 | 54 | 223 | 307 | 17 | 0.55 | 188 | 345 | — | — | Well eaten |
| Combination pump—Port—Top | 40 | 51 | 16 | 35 | 93 | 126 | 8 | 0.6 | 80 | 149 | — | — | Well eaten |
| Bottom | — | — | — | — | 86 | 125 | 10 | 0.8 | 78 | 144 | — | — | Well eaten |
| Downtown pump—Port—Top | 40 | 51 | 16 | 35 | 81 | 108 | 9 | 8 | 74 | 136 | 51 | 0.7 | Well eaten |
| Bottom | — | — | — | — | 93 | 118 | 9 | 0.7 | 80 | 131 | 17 | 0.2 | Poorly eaten |
| Evap. blowdown—Port | Missing | | | | 30 | 38 | 7 | 1.6 | 20 | 41 | — | — | Well eaten |
| After mag. flooding—Stbd. | 50 | 63 | 40 | 23 | 144 | 214 | 11 | 0.55 | 120 | 278 | — | — | Fairly well eaten |
| Condenser discharge—Stbd. | 91 | 126 | 48 | 78 | 209 | 284 | 14 | 0.5 | 174 | 248 | — | — | Fairly well eaten |
| Fire and bilge pump—Stbd. | 40 | 51 | 35 | 16 | 169 | 244 | 8 | 0.35 | 145 | 291 | 79 | 0.55 | Fairly well eaten |
| Discharge fire and bilge—Stbd. | 13 | 15 | 8 | 7 | 55 | 99 | 5 | 0.65 | 49 | 107 | — | — | Very well eaten |
| Sanitary pump—Stbd. | — | — | — | — | 62 | 86 | 6 | 0.7 | 50 | 100 | — | — | Well eaten |
| Main injection—Stbd. | — | — | — | — | 345 | 546 | 36 | 0.75 | 300 | 610 | — | — | Well eaten |
| Inside eddy plates—On hull | 94 | 174 | 138 | 36 | | | | | 98 | 193 | — | — | Not seen |
| Stbd. On plate | 76 | 143 | 93 | 50 | Not fitted | | | | Not fitted | | | | |
| On plate | 82 | 152 | 115 | 37 | | | | | | | | | |
| On plate | 72 | 137 | 120 | 17 | | | | | | | | | |
| Inside eddy plates—On hull | 94 | 174 | 154 | 20 | | | | | 100 | 184 | — | — | Not seen |
| Port On plate | 71 | 134 | 86 | 48 | | | | | | | | | |
| On plate | 85 | 139 | 118 | 21 | Not fitted | | | | Not fitted | | | | |
| On plate | 55 | 124 | 114 | 10 | | | | | | | | | |
| On plate | 68 | 128 | 107 | 21 | | | | | | | | | |
| Totals | 1959 | 3861 | 2376 | 1485 | 2567 | 4304 | 254 | — | 2427 | 5068 | | | |

been different. But many of the contributing factors would be common, and since differences would generally be in degree rather than in effect, the results and recommendations could be applied, with discretion, to the different cases, both in regard to naval and merchant shipping.

As indicated by the surveys on *Quinte*, a ship has three main cathodic 'sinks' which promote the corrosion of the bare steel occurring on its hull, unless the exposed steel is protected by a source of greater anodic activity. These cathodic 'sinks' occur at (*a*) the painted steel areas, (*b*) the bronze propellers, (*c*) the water line. Other cathodic sinks, such as the bronze fittings at outlets and areas of steel coated with millscale, were found to be subordinate. The order of importance of (*a*), (*b*), and (*c*) in promoting corrosion depends on the condition of the hull, and is determined by such factors as the activity of the protecting anodes, the degree of polarization, the type and age of paint film, the thickness of various deposits, and the area of exposed steel.

These large scale experiments have shown that an appreciable current may flow from bare to painted steel. An intact paint film, if of sufficiently high resistance, will considerably reduce corrosion by simply imposing an ohmic resistance barrier between anode and cathode. A paint film of low resistance will protect the area over which it is intact, but stimulates corrosion of the uncovered patches. Paints are frequently applied over rusty or poorly prepared surfaces and hence form only a relatively low resistance barrier to the passage of current. In addition, common types of underwater paints even when applied to prepared surfaces have very low specific resistances after a short period of immersion in sea water.

The effects of this current flow may explain the rapid corrosion of rivets noted on many Canadian warships. Rivets that had an intact coating of paint were not rusted (since they would tend to act as cathodes), but rivets that had no paint covering were usually badly rusted, even though the steel plates (painted) in the immediate vicinity were not. As rivets project from the sides of the ship they are very liable to get a thinner coating, when painted by brushing, than are the surrounding flat steel plates and, on account of their projection, the paint is more liable to be worn off before that of the plates. Hence a condition develops that is conducive to a current flow from the rivets to the paint surface, and the rivets tend to corrode rapidly.

It is well known that a current will flow between steel and bronze (propellers) in metallic contact. As indicated by the results of the surveys, the corrosive effects of this current are most detrimental when a ship is just out of drydock, with small unpainted holidays (e.g., at bilge and keel block positions), a generally intact coat of paint, bronze propellers that have been cleaned and no, or poorly fitted, zincs. In this case the current from the hull is confined to the small areas of bare steel and causes excessive pitting at these places (see Fig. 25). Also, all ships under service conditions are subject to damage to the paint near the water line, hence some method to supplement

painting should be used to protect this area from the action of the hull-to-propeller current. The effect of this galvanic couple will be greater for a ship underway than at rest because of depolarization of the bronze by agitation and possible effects from water moving at different speeds over steel. The current to the propellers decreased with increased chalking of them. Hence the effects of this cause of corrosion tend to decrease with time, and would be further diminished if the propellers could be insulated from the hull, coated with an impervious film, or made from (or coated with) a material having a similar potential to that of the hull.

The effect of the water line cathodic region, induced by differential oxygen concentration and intermittent air exposure, assumed a relatively more important role with increase in the area of bare steel on the underwater hull.

Areas of millscale on steel will stimulate the corrosion of the bare steel and, if of sufficient size, may cause considerable pitting. On *Quinte*, with exception of the starboard 'A' bracket, no noticeable amount of millscale was present, and after sandblasting none was present.

One of the most influential factors in preventing excessive corrosion is the effect of cathodic polarization, which reduces the intensity of the corrosion currents. In the survey of *Quinte* following its exposure to air, it was shown that the magnitude of both anodic and cathodic potential differences was much smaller after polarization had been reestablished than when the ship was in the unpolarized state immediately after undocking.

Polarization also reduces the current requirements for 'cathodic protection'. Cathodic protection of ships has been recommended by many, but, up to the present, main reliance has been placed on paint films to protect the hulls against corrosion, and cathodic protection has been applied only in a subordinate manner by the use of small zinc anodes. The zincs are fastened close to the bronze propellers and at outlets that have bronze fittings, in an attempt to supply the bronze with current from the zincs, instead of from the adjacent steel. When securing the zincs to the hull, no provision is made for maintenance of a waterproof metal-to-metal contact and, contrary to good shipbuilding practice, frequently rusted nuts and bolts, or bronze screws, are used in fastening. Consequently in many instances the metallic contact rapidly deteriorates and the protection fails. Moreover it has been shown with *Quinte* that even though a sufficient number of well fitted zincs would cathodically protect a ship, the corrosion products that formed on the zinc surface would reduce the current below the value required for cathodic protection in a relatively short time (the order of a month). Hence for adequate cathodic protection, measures other than the above should be investigated and applied.

Deposition films on the cathodes (e.g., on the propellers) act in a somewhat similar manner to paint films in reducing corrosion in that they impose resistance barriers and reduce the current density required for polarization. Cathodic protection accelerates the deposition of these films.

The poor performance of the proprietory bituminous-based paint used, both on *Quinte* and in the laboratory, indicated that it is unsatisfactory for use as an underwater paint. Although some of the flaking may have resulted from the passage of current applied 68 days after the fourth drydocking, it is considered that failure was due primarily to its brittleness and its property of extremely poor adherence to clean steel. On drying, the paint became even more brittle and lifeless and many flakes were removed from the steel by the wind. The paint clung to rivet heads and flaked from flat surfaces, in contradiction of the normal state in which the common underwater paints tend to leave the rivets first. This is explained by the care that was taken to apply the paint liberally to the rivets whose roughened surfaces allowed the paint a better mechanical grip than did flat plates. Hence the paint on the rivets could withstand slightly more strain than that on the flat surface of the steel.

It is apparent that there are weaknesses in the present anticorrosion technique used on ships which may result in excessive corrosion. The use of zinc anodes for cathodic protection is unsatisfactory, since they do not remain active throughout the time of service between drydockings. Little is done towards eliminating the current to the propellers. The paint film in general use is of low resistance and is often applied over poorly prepared surfaces. Holidays are left in the paints at bilge and keel block positions and, unavoidably, the paint film is damaged when the ship is at berth. Apart from preventing fouling, a paint film can be worse than none, as it may result in excessive pitting of the bare steel at holidays. It should be remarked that Canadian anticorrosive technique is similar to that of Admiralty, with the exception of the different types of paints used. No direct experience has been had here with the plastic paints of Admiralty or of U.S. Navy manufacture, but it is understood that the U.S.N. paints have given very satisfactory service on one of the R.C.N. ships.

The following suggestions are offered for improving anticorrosion technique: (*a*) more intensive use of cathodic protection; (*b*) the use of an improved underwater paint; (*c*) better preparation of surfaces for painting; (*d*) more careful painting of rivet heads; (*e*) coating the bronze propellers with an impervious, adherent paint film, or a less cathodic metal, or insulating them from the hull.

Of the above, (*a*) is considered the most important. Under service conditions, damage to paint films is bound to occur, even though the films were perfect in every respect when applied, and these damaged places need protection if rusting is to be prevented. In practice, the perfect paint film is not attained, nor would it be necessary if cathodic protection were used to a sufficient degree, although, with a better paint film, the average current density required would be lower.

The general properties of the paint should be such that it forms a tough, non-brittle film that adheres well to a prepared steel surface, has a high electrical resistance, and will withstand the stresses caused by the application of the protecting current. Although no paint film can be expected to withstand the severe abrasion at jetties, it should be capable of withstanding light

abrasion. The high electrical resistance is desirable to reduce the passage of current through the paint to a negligible amount. This is a more important requirement if cathodic protection is not used and the painted steel is cathodic to bare steel. Experiments concerning the electrical behavior of paint films have shown that many paints strip under the action of the protecting current. Other such experiments are required to determine the best type of coating to use with cathodic protection. The stripping of the paint films by the protecting current is not of great importance if corrosion alone is the main problem, e.g., for decommissioned ships, but where fouling of the ship is of primary consideration (as for active ships in tropical waters) paint stripping is serious, since present antifouling technique depends on the special properties of certain paints.

A well prepared surface is essential if the paint is to exhibit best its adherent and high-resistance properties. Otherwise, a break in the film may allow water to seep behind the paint. To provide a better surface preparation, a wet sandblasting technique has become standard practice in the U.S. Navy and is also used to some extent by Admiralty, but has not been tried by the Canadian Navy. The careful coating of the rivets and the elimination of current to the propellers are of less consequence when cathodic protection is used.

As improvements in the technique of cathodic protection, the following possibilities present themselves:

(*a*) The use of a different metal to replace zinc as a sacrificial anode. Corrosion products either should not form on the surface of the metal, or should be readily removable and have a very low resistance to the passage of current from the anode.

(*b*) The use of a larger anode area in conjunction with either (i) depolarizers that will prevent the formation of the corrosion products on the anode surface, or (ii) periodic cleaning of the anode surface to remove the corrosion products.

(*c*) The use of an anode energized by an adjustable external source (e.g., battery or low voltage generator). This should give better control in that the average current density could be altered to suit requirements, i.e., with increase in damage to the paint film, the total protective current could be augmented.

Service conditions must be taken into consideration when deciding on the source of current. For instance, where nearby power sources are unavailable, decommissioned ships could be protected more conveniently by suitable sacrificial anodes suspended from the ship. If an increase in current were required, another anode could be readily added. For ships in active service, however, any anode must be rigidly attached to the hull, and addition of anodes would be difficult, except in drydock. But as these ships have electrical power available, system (*c*) might be used to advantage.

It is evident from the surveys of *Quinte*, that the current from an actively protecting anode spreads over a considerable area and is not confined to the

immediate area around the anode. (This is well shown in Fig. 9.) Thus even though anodes were not placed in the immediate vicinity of the bronze fittings, the steel near such fittings would not rust if the hull had full cathodic protection. The anodes may, therefore, be positioned with regard to ease of fastening, which will permit a better connection, rather than to nearness to the numerous outlets. It is, however, desirable to have more than one anode, since the current density over a large cathode (i.e., the hull) will decrease somewhat with distance from the anode.* But the variation does not warrant the present practice of scattering small anodes over the hull, often where it is difficult to fit them (e.g., recessed or re-entrant places). For many ships, the long, flat surfaces of the bilge keels would provide convenient positions to fit the anodes. The dimensions of the anodes could then conform with the dimensions of the ship (long and narrow) minimizing the variations in distance between anode and cathode, and placing the anode relatively close to regions requiring greater protection, e.g., bare steel areas near the water line. In all cases the anodes should be fitted with permanent waterproof connections.

When cathodic protection is used as a means of rust prevention, the optimum current value will usually increase with time owing to the abrasion of the covering film exposing an increasing amount of steel. Normally the rate of increase will be dissimilar for any two ships, making necessary a criterion of how much current should be applied at a given time. Preliminary experiments indicated the possibilities of a rather simple test as to the efficacy of a given current flow at any time by measuring the potential of the hull with respect to a standard reference electrode, the reference electrode being held at least 30 ft. from the hull. The value of the potential for optimum current flow will depend on the system used for cathodic protection, and needs to be determined by experience.

## Conclusions

By investigating the electrical potential differences in the sea in the immediate vicinity of a steel ship, it has been shown that:

(1) The corrosion history of the steel ship may be followed in reasonable detail by making potential surveys in the sea surrounding the ship.

(2) The chief cathodic sinks occur at (*a*) painted steel areas, (*b*) bronze propellers, (*c*) water line.

(3) Cathodic protection of a ship appears practical, particularly where corrosion is the main problem (e.g., reserve ships). A rather low current requirement is indicated, less than 30 amp. for a Bangor Class Minesweeper, or an average of less than 6 ma. per sq. ft.

(4) The current from an active anode spreads over a considerable area and is not confined to the immediate vicinity of the anode.

(5) Zinc is not satisfactory as a sacrificial anode for cathodic protection in sea water.

**To be discussed in a later report.*

## Acknowledgments

The work described in this paper arose out of suggestions made by the British Admiralty, and close liaison has been maintained throughout. Agreement of the Defence Research Board, and of Admiralty, to the publication of this paper is acknowledged.

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[Figs. 1 to 27 follow.]

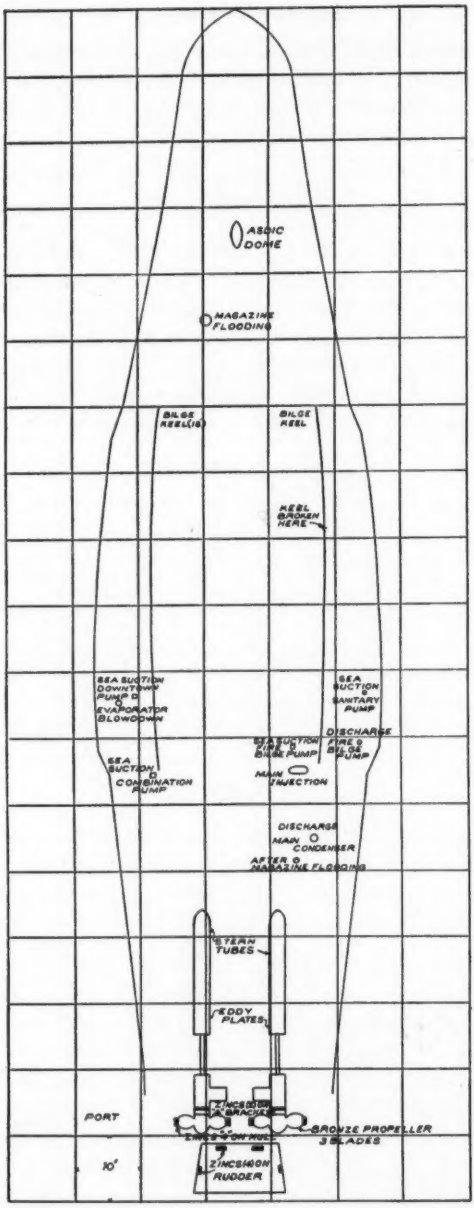


FIG. 1. *Expanded outline of the underwater hull, showing relative positions of underwater outlets and fittings.*

*Outline drawn for ship when drafts were 7¼ ft. forward and 9¼ ft. aft.*

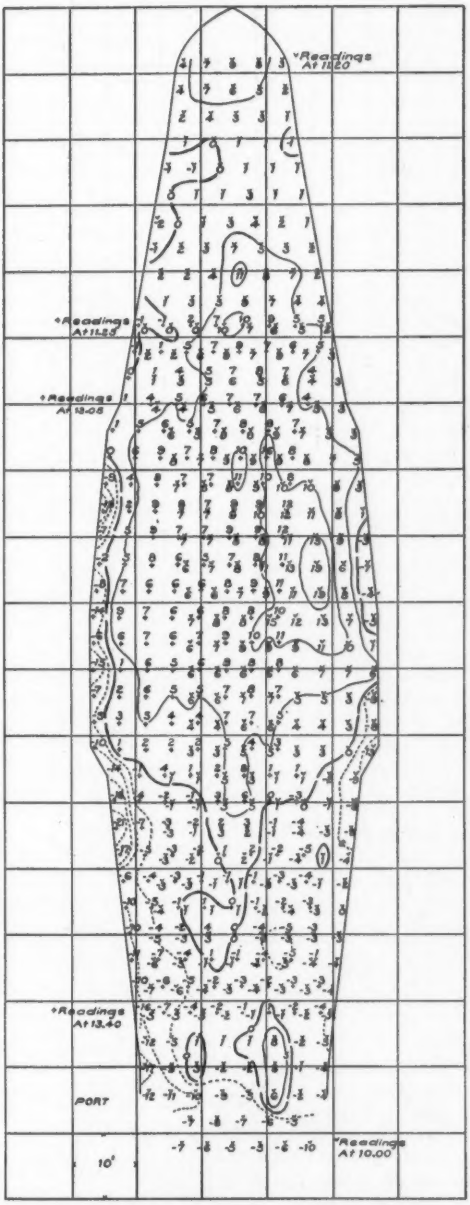


FIG. 2. *Results of survey on March 15, 1946.*
*Weather —Sunny. Temp. 30° to 47° F. Moderate wind.*
*Sea —Choppy.*
*Remarks—Ship yawed severely during survey.*
*Last drydocking—July 4-6, 1944.*

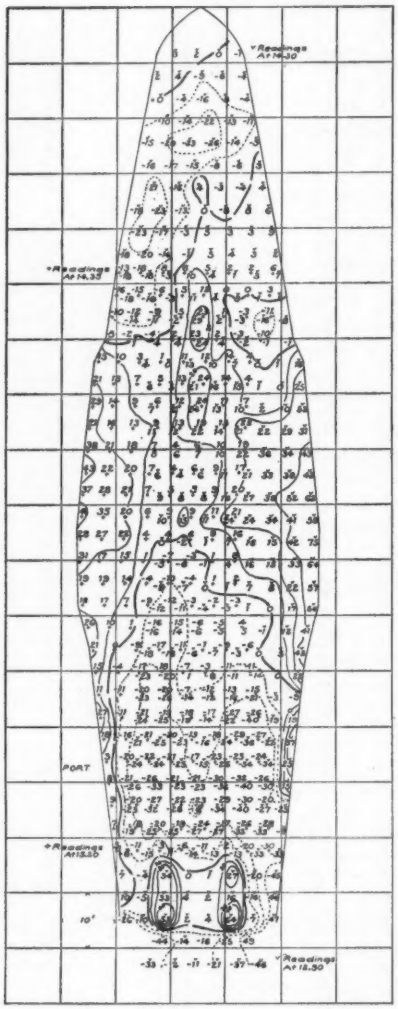


FIG. 3.

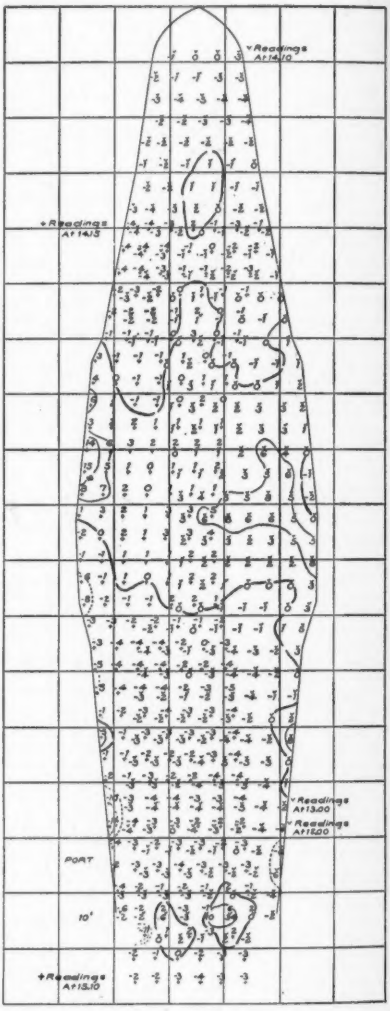


FIG. 4.

FIG. 3. *Results of survey on March 22, 1946.*
*Weather —Sunny. Temp. 34° to 58° F. Moderate wind.*
*Sea —Choppy.*
*Remarks—Ship yawed during survey.*
*Last drydocking—March 20-22 (1000 hr.), 1946.*

FIG. 4. *Results of survey on April 6, 1946.*
*Weather —Cloudy. Temp. 31° to 37° F. Moderate wind.*
*Sea —Choppy, 2 ft. waves.*
*Remarks—Ship yawed severely.*
*Last drydocking—March 20-22, 1946.*

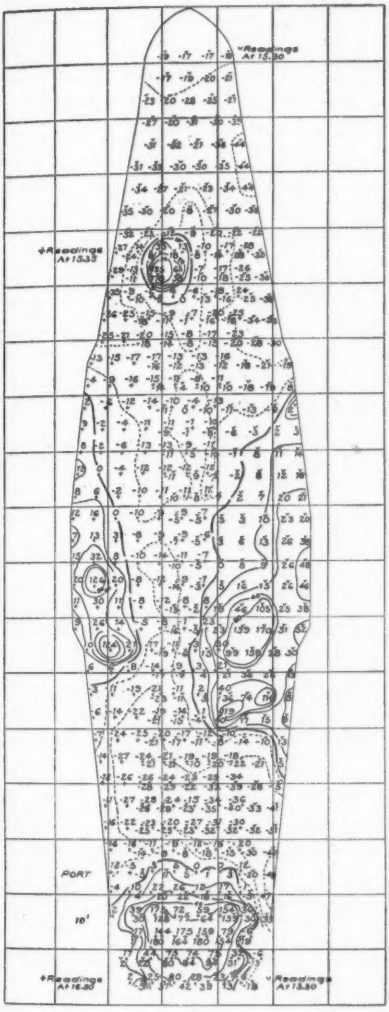


FIG. 5.

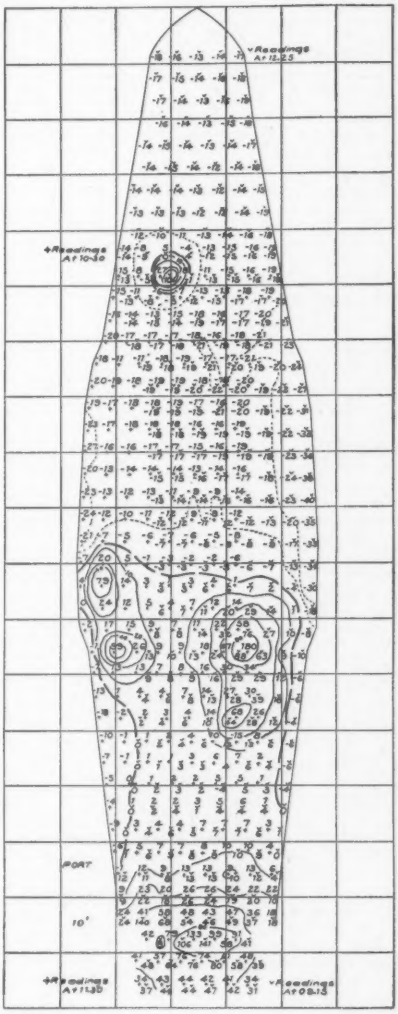


FIG. 6.

FIG. 5. *Results of survey on April 9, 1946.*
*Weather —A.m. clearing, p.m. sunny. Temp. 30° to 39° F. Strong wind.*
*Sea —1 to 2 ft. waves.*
*Remarks—Ship was secured by stern and it held steady.*
*Ship was secured in this manner for all subsequent surveys.*
*Last drydocking—April 7-9 (1200 hr.), 1946.*

FIG. 6. *Results of first survey on April 26, 1946.*
*Weather —Light to heavy rain. Temp. 36° to 52° F. Strong wind.*
*Sea —½ to 1 ft. waves.*
*Remarks—This survey was taken just prior to the passage of depolarizing current. (see Fig. 7)*
*Last drydocking—April 7-9, 1946.*

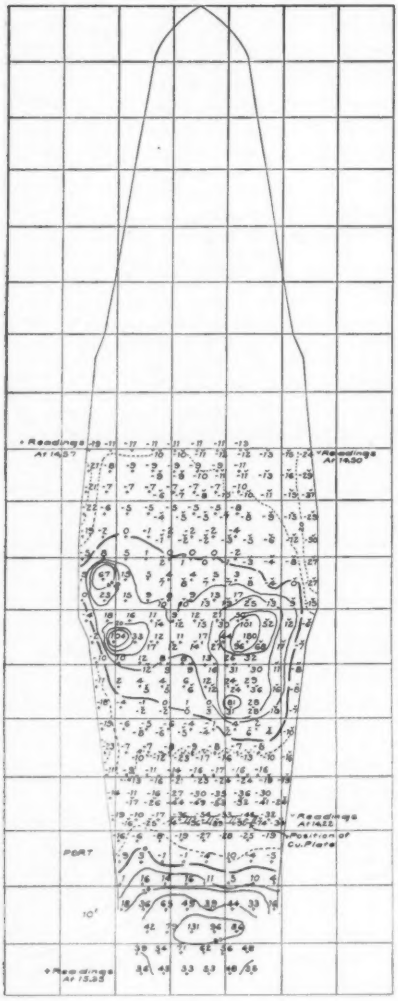


FIG. 7.

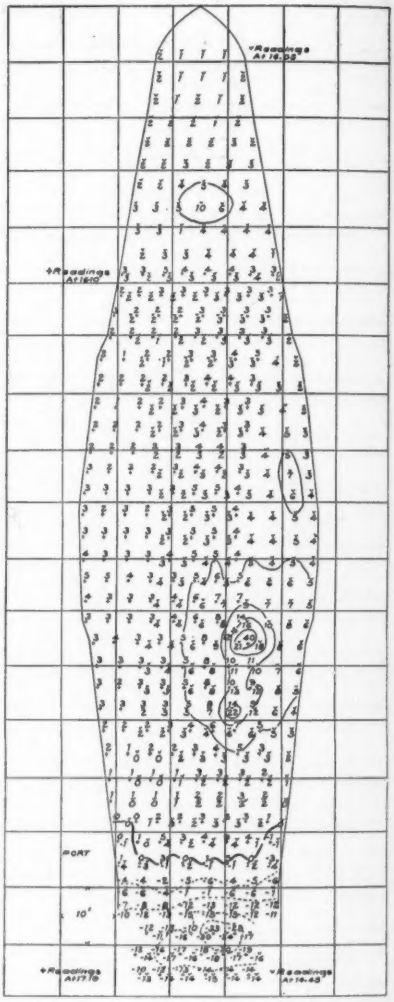


FIG. 8.

FIG. 7. *Results of second survey on April 26, 1946.*
*Weather —Heavy rain. Temp. 36° to 52° F. Strong wind.*
*Sea —¼ to 1 ft. waves.*
*Remarks—This survey was taken just after a depolarizing charge of approximately 45 amp-hours had flowed from the hull to a copper plate placed about 32 ft. from the stern.*
*Last drydocking—April 7-9, 1946.*

FIG. 8. *Results of survey on May 18, 1946.*
*Weather —Light rain. Temp. 40° to 46° F. Strong wind.*
*Sea —¼ to 1 ft. waves.*
*Last drydocking—April 30-May 18 (1135 hr.), 1946.*

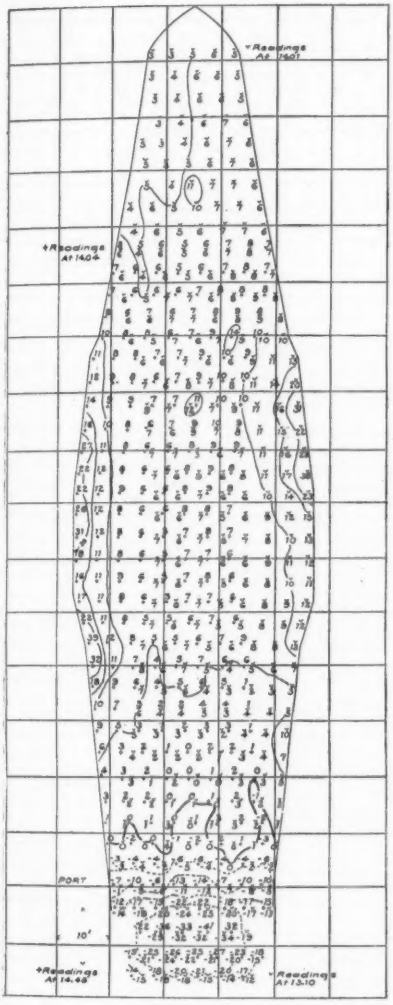


FIG. 9.

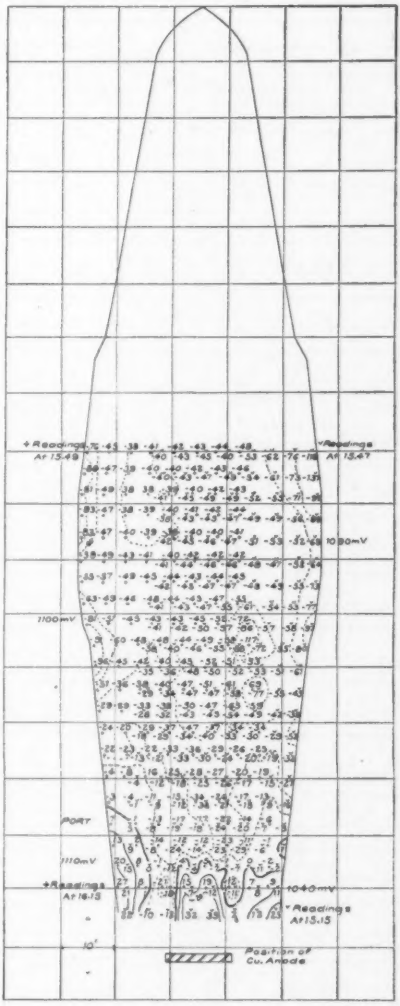


FIG. 10.

FIG. 9. *Results of initial survey on May 27, 1946.*
*Weather —Overcast with intermittent rain. Temp. 50° to 60° F. Slight breeze.*
*Sea —Calm.*
*Remarks—Survey made prior to passing of current.*
*Last drydocking—April 30-May 18, 1946.*

FIG. 10. *Results of second survey on May 27, 1946.*
*Remarks—Survey was carried out while an applied current of about 30 amp. was being passed to the hull from an external anode (copper plate). Also shown is the increase in value of the e.m.f. of the hull with respect to a silver – silver chloride electrode, with time, i.e., passage of current. (The readings were taken using an Avo-Meter 12 v. scale, the hull being connected to the negative terminal of the meter).*

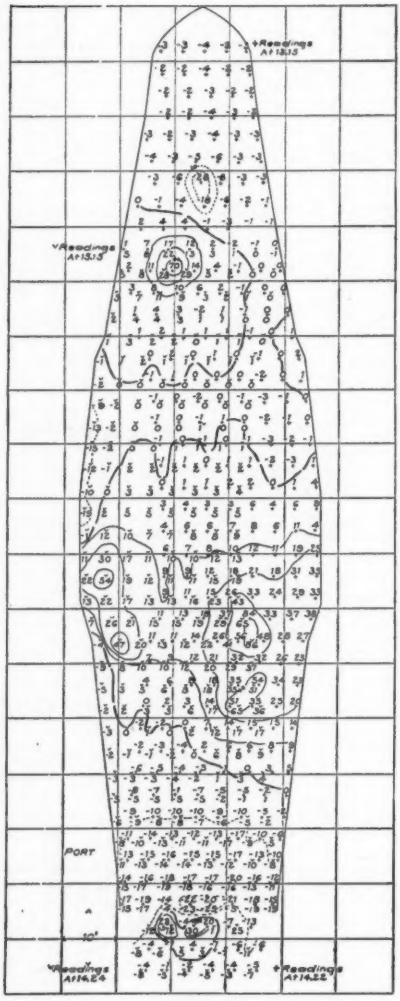


FIG. 11.

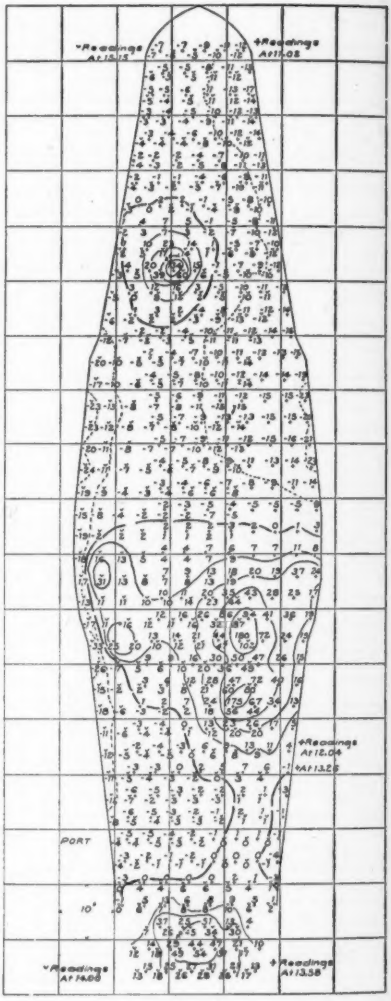


FIG. 12.

FIG. 11. *Results of survey on May 30, 1946.*
*Weather—Clear. Temp. 45° to 55° F. Light wind.*
*Sea —Calm in a.m. ¼ ft. waves in p.m.*
*Last drydocking—May 29, 1946.*

FIG. 12. *Results of survey on July 2, 1946.*
*Weather—Foggy in a.m. Drizzle in p.m.*
*Temp. 60° to 70° F. Strong wind in p.m.*
*Sea —1 to 2 ft. waves.*
*Remarks—Ship had been berthed starboard side next the jetty for a few ays since last survey.*
*Last drydocking—May 29, 1946.*

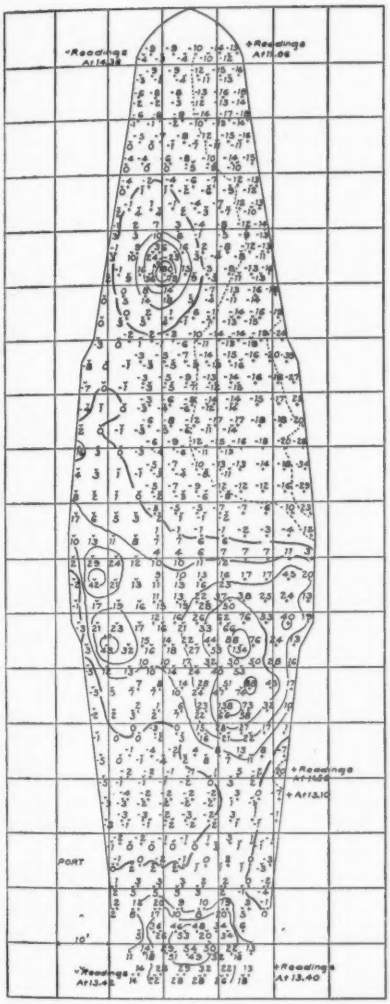


FIG. 13.

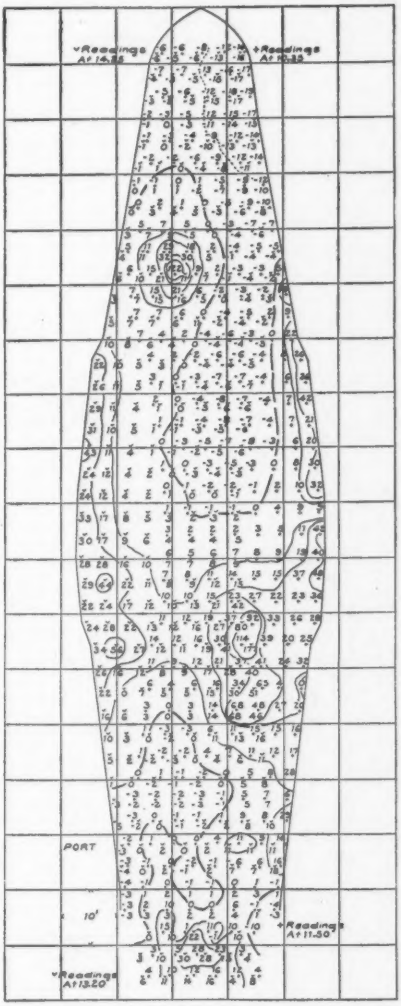


FIG. 14.

FIG. 13. *Results of survey on July 4, 1946.*
*Weather —Fine. Temp. 60° to 80° F. Slight breeze.*
*Sea —Rippled.*
*Remarks—The propellers were cleaned by divers on July 3, 1946.*
*Last drydocking—May 29, 1946.*

FIG. 14. *Results of survey on August 2, 1946.*
*Weather —Overcast. Temp. 55° to 65° F. Moderate wind.*
*Sea —1 ft. waves.*
*Last drydocking—May 29, 1946.*

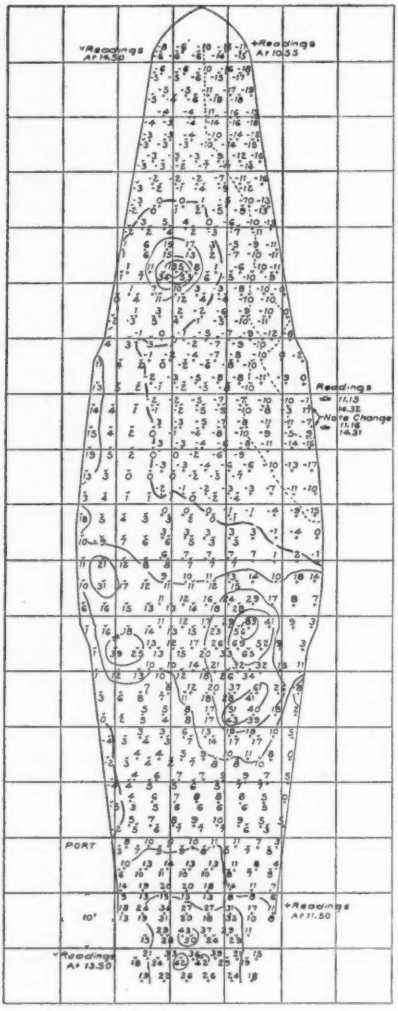


FIG. 15.

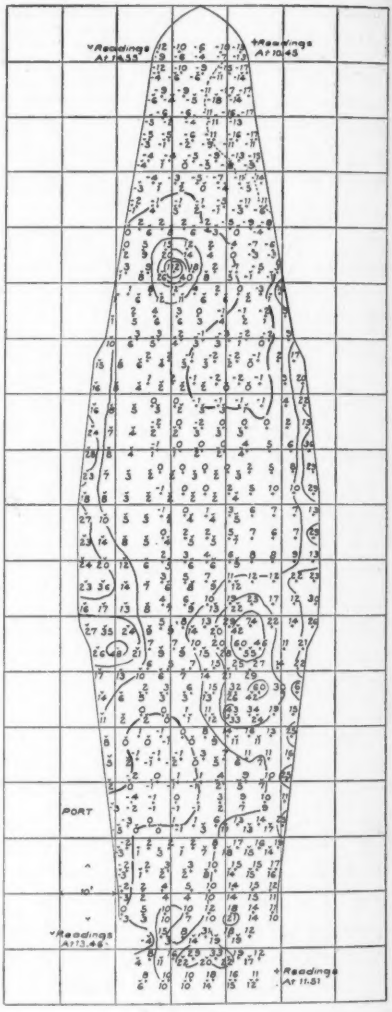


FIG. 16.

FIG. 15. *Results of survey on August 5, 1946.*
*Weather —Foggy in a.m. Fine in p.m. Temp. 60° to 70° F. Light wind.*
*Sea —Calm.*
*Remarks—Current of 30 amp. passed for 50 hr. from a copper electrode to hull, prior to this survey.*
*Last drydocking—May 29, 1946.*

FIG. 16. *Results of survey on August 12, 1946.*
*Weather —Foggy in a.m. Fine in p.m. Temp. 65° to 80° F. Light breeze.*
*Sea —¼ ft. waves.*
*Last drydocking—May 29, 1946.*

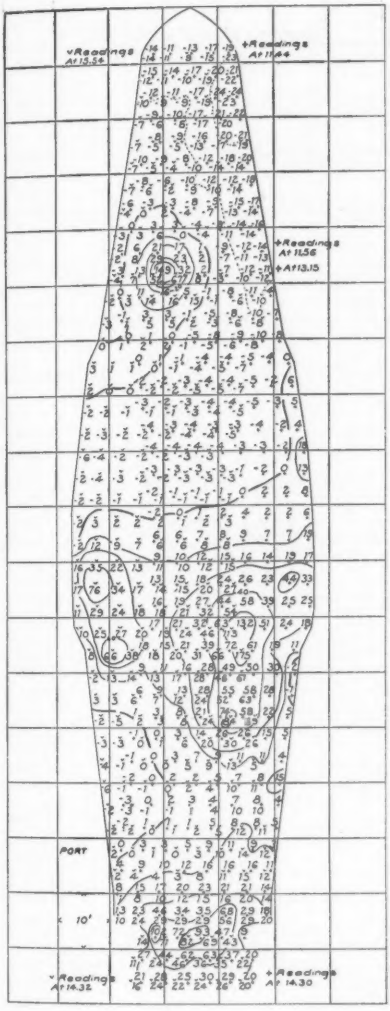


FIG. 17.

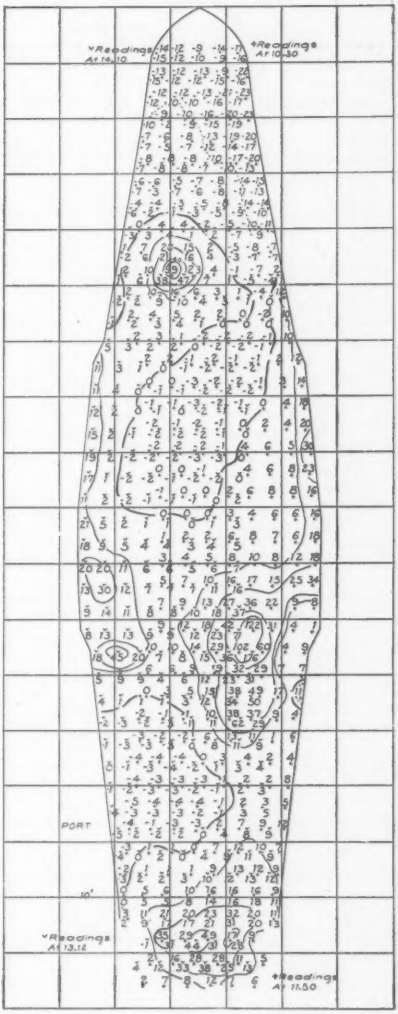


FIG. 18.

FIG. 17. *Results of survey on August 14, 1946.*
*Weather—Rain. Temp. 55° to 65° F. Light wind.*
*Sea —Calm.*
*Remarks—The zincs had been cleaned by diver prior to survey.*
*Last drydocking—May 29, 1946.*

FIG. 18. *Results of survey on August 21, 1946.*
*Weather—Heavily overcast. Temp. 55° to 70° F. Light wind.*
*Sea —Calm.*
*Last drydocking—May 29, 1946.*

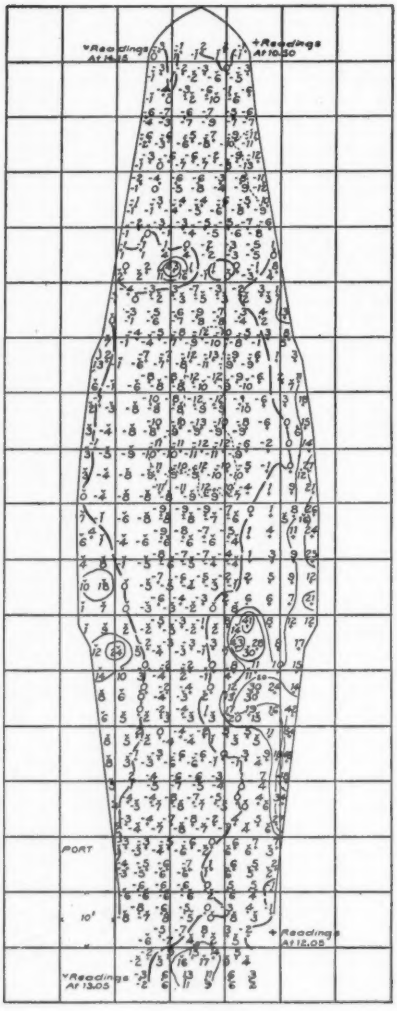


FIG. 19.

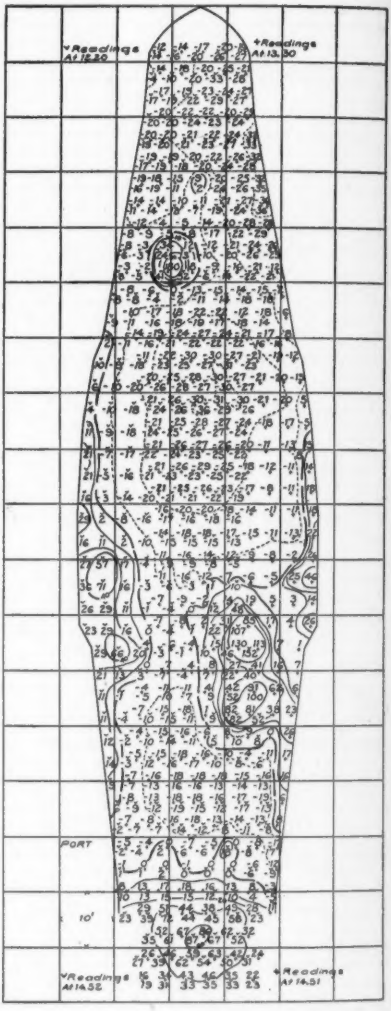


FIG. 20.

FIG. 19. *Results of survey on October 28, 1946.*
*Weather—Fine. Temp. 45° to 60° F. Moderate wind.*
*Sea —1 ft. waves in a.m. ½ ft. waves in p.m.*
*Remarks—A dead ship. Decommissioned Oct. 25, 1946.*
*Last drydocking—May 29, 1946.*

FIG. 20. *Results of survey on October 30, 1946.*
*Weather —Overcast. Temp. 45° to 60° F. Moderate wind, decreasing in p.m.*
*Sea —2 ft. waves in a.m. 1 ft. waves in p.m.*
*Remarks—A dead ship.*
*Last drydocking—October 29-30 (1130 hr.), 1946.*

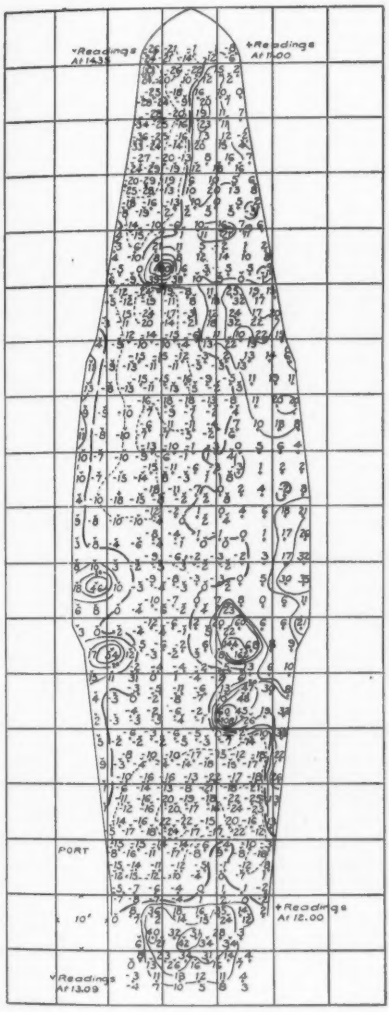


FIG. 21.

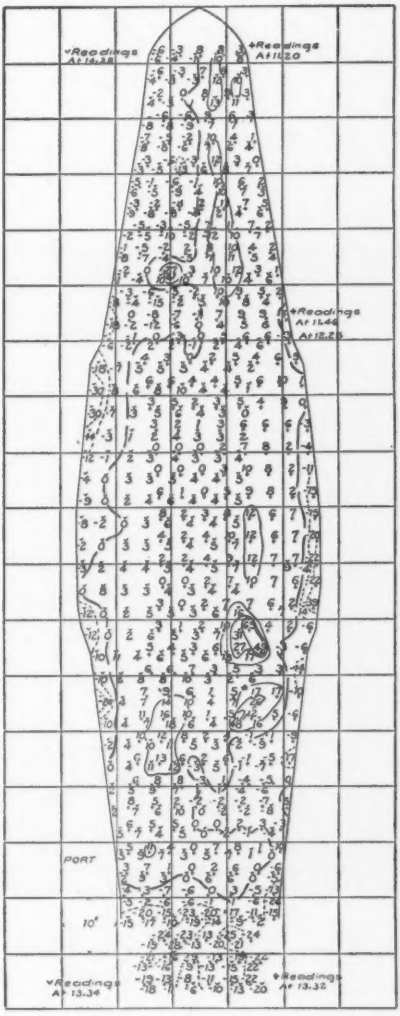


FIG. 22.

FIG. 21. *Results of survey on November 1, 1946.*
*Weather —Scattered showers. Temp. 40° to 55° F. Strong wind.*
*Sea —2 to 3 ft. waves.*
*Remarks—A dead ship.*
*Last drydocking—October 29-30, 1946.*

FIG. 22. *Results of survey on December 11, 1946.*
*Weather —Clear. Temp. 35° to 45° F. Strong wind.*
*Sea —3 ft. waves.*
*Remarks—A dead ship. Had just completed winterization prior to this survey.*
*Last drydocking—October 29-30, 1946.*

For Figs. 23 to 27 (PLATES I to V) see the following inserts.

PLATE I

FIG. 23. *Showing the general appearance of rusting near water line due to removal of the paint film by abrasion at jetties. Photograph was taken April 7, 1946.*

PLATE II

FIG. 24. *Showing the general appearance of pitting due to removal of the paint film near the water line by abrasion. Photograph was taken after the hull had been sandblasted and painted with anticorrosive paints.*

FIG. 25. *Showing the general appearance of the severe pitting present at the unpainted bilge block positions prior to May 1946. The photograph was taken after the hull had been sandblasted and painted with anticorrosive paints.*

FIG. 26. *Showing the general appearance of rusting at the bow at regions where the paint film had flaked off the hull. This flaking was primarily due to the extreme brittleness of the bituminous paint. Photograph was taken soon after the ship was drydocked on October 29, 1946.*

PLATE V

FIG. 27. *Showing the general appearance of the zinc anodes at the after magazine flooding valve. Photograph was taken just after the zincs had been cleaned with a small wire hand-brush on October 29, 1946. (+, Studs that had been coated with ozite).*